GLOBAL PETROLEUM RESEARCH INSTITUTE
TEXAS A&M ENGINEERING EXPERIMENT STATION

Department of Petroleum Engineering
Texas A&M University

Report Title: **PILOT TESTING: PRETREATMENT OPTIONS TO ALLOW RE-USE OF FRAC FLOWBACK AND PRODUCED BRINE FOR GAS SHALE RESOURCE DEVELOPMENT**

Type of Report:	Final Report
Reporting Period Start Date:	October 1, 2009
Reporting Period End Date	December 31, 2012
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Issued	September, 2014
DOE Award Number	**DOE NETL DE-FE0000847**
Submitting Organization	Texas A&M University College Station, Texas
	New York State Research Development Authority Albany, NY
	Sam Houston State University Huntsville TX.
	Argonne National Laboratory Washington D. C.
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Abstract

The goal of the A&M DOE NETL Project No. **DE-FE0000847** was to develop a mobile, multifunctional water treatment capability designed specifically for "pre-treatment" of field waste brine. The project consisted of constructing s mobile "field laboratory" incorporating new technology for treating high salinity produced water and using the lab to conduct a side-by-side comparison between this new technology and that already existing in field operations.

A series of four field trials were performed utilizing the mobile unit to demonstrate the effectiveness of different technology suitable for use with high salinity flow back brines and produced water. The design of the mobile unit was based on previous and current work at the Texas A&M Separation Sciences Pilot Plant. The several treatment techniques which have been found to be successful in both pilot plant and field tests had been tested to incorporate into a single multifunctional process train. Eight different components were evaluated during the trials, two types of oil and grease removal, one BTEX removal step, three micro-filters, and two different nanofilters. The performance of each technique was measured by its separation efficiency, power consumption, and ability to withstand fouling.

The field trials were a success. Four different field brines were evaluated in the first trial in New York. Over 16,000 gallons of brine were processed. Using a power cost of $.10 per kWh, media pretreatment power use averaged $0.004 per barrel, solids removal $.04 per barrel and brine "softening" $.84 per barrel. Total power cost was approximately $1.00 per barrel of fluid treated.

In Pennsylvania, brines collected from frac ponds were tested in two additional trials. Each of the brines was converted to an oil-free, solids-free brine with no biological activity. Brines were stable over time and would be good candidates for use as a make-up fluid in a subsequent fracturing fluid design.

Reports on all of the field trials and subcontractor research have been summarized in this Final Report. Individual field trial reports and research reports are contained in the companion volume titled "Appendices"

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Abbreviations/Acronyms

BETX	Benzene, Ethylbenzene, Toluene, Xylene
EFD	Environmentally Friendly Drilling
HARC	Houston Advanced Research Center
LANL	Los Alamos National Laboratory
PTTC	Petroleum Technology Transfer Council
TAMU	Texas A&M University
TEEX	Texas Engineering Extension Service

PILOT TESTING: PRETREATMENT OPTIONS TO ALLOW RE-USE OF FRAC FLOWBACK AND PRODUCED BRINE FOR GAS SHALE RESOURCE DEVELOPMENT

Final Report; 2009 - 2012

Executive Summary

The goal of the A&M DOE NETL Project No. DE-FE0000847 has been to develop a mobile, multifunctional water treatment capability designed specifically for "pre-treatment" of field waste brine. The project consists of conducting a side-by-side comparison between this new technology and that already existing in field operations.

Field trials utilized a mobile unit to demonstrate the effectiveness of different technology suitable for use with high salinity flow back brines and produced water. The design of the mobile unit is based on previous and current work at the Texas A&M Separation Sciences Pilot Plant. The several treatment techniques which have been found to be successful in both pilot plant and field tests had been tested to incorporate into a single multifunctional process train. Eight different components were evaluated during the trials, two types of oil and grease removal, one BTEX removal step, three micro-filters, and two different nanofilters. The performance of each technique was measured by its separation efficiency, power consumption, and ability to withstand fouling.

Four field trials were conducted with the unit over a two-year period. The first test was in South Texas in the Eagle Ford Shale and served as a trial run of the unit that had just been constructed. The second trial was in upstate New York in Chenango County at a Norse Energy site. The unit tested produced waters from the Herkimer Silurian formation that served as analogs to Marcellus Shale brine. The tests were performed on these brines because of the moratorium on Marcellus Shale drilling in New York. The third and fourth trials were conducted in Pennsylvania, one in Washington County at a Range Resources site, the other in Worthington County at a BG – Exco Resources partnership site. The last three trials were extended duration tests to demonstrate that pre-treatment of ultra-high salinity brines could be accomplished successfully and in a cost effective manner.

The field trials were a success. Four different field brines were evaluated in the first trial in New York. Over 16,000 gallons of brine were processed. Using a power cost of $.10 per kWh, media pretreatment power use averaged $0.004 per barrel, solids removal $.04 per barrel and brine "softening" $.84 per barrel. Total power cost was approximately $1.00 per barrel of fluid treated.

In Pennsylvania, brines collected from frac ponds were tested in additional trials. Each of the brines was converted to an oil-free, solids-free brine with no biological activity. Brines were stable over time and would be good candidates for use as a make-up fluid in a subsequent fracturing fluid design.

Pilot Testing: Pretreatment Options to Allow Re-Use of Frac Flowback and Produced Brine for Gas Shale Resource Development

Introduction

Background and Justification for the Project

Shale gas development relies heavily on the hydraulic fracturing process in order to maximize the economic viability of each new well. The challenge is to identify technologies and approaches for treating the frac water that returns to the surface following a frac job (frac flowback water) for beneficial re-use in other applications, thereby conserving other local freshwater supplies. In the Marcellus Shale the technology used must be able to accommodate ultra-high salinity brine concentrations and have the ability to remove hydrocarbons, suspended solids including bacterial activity, and scaling minerals and materials that would be detrimental to fracturing fluid chemicals if used as make up brine.

Goals and Objectives of the A&M Project

The goal of the A&M Program was to develop a mobile, multifunctional water treatment capability designed specifically for "pre-treatment" of field waste brine by conducting a side-by-side comparison between this new technology and that already existing in field operations.

The objective of the project has been to identify appropriate technology for brine treatment and to demonstrate the technology in field trials. The specific task objectives were to be accomplished in sequential steps to demonstrate frac water pre-treatment technology's ability to remove constituents from the high salinity flowback water and produced brines encountered in the Marcellus region. The specific objectives should be accomplished with minimal chemical usage and no adverse environmental impact.

To accomplish this, the A&M team with its partners, tested a number of processes designed to remove contaminants from highly saline brines. Once components of a process train were identified and tested, a mobile testing laboratory was designed and constructed to allow extended duration tests to be conducted in the field.

A comprehensive analytical test program was planned to provide on-site monitoring of the process. An additional objective, required because of the unavailability of brine from Marcellus wells, was to identify, then test ultra-high salinity brines from the Herkimer formation. Herkimer wells, producing from the Silurian geologic trend represented an analog to Marcellus brine. An extra incentive to test the Herkimer formation is that information from these brines can be used to characterize the Utica Shale brines.

As the program has matured, a new goal has been identified, to seek out and utilize the most appropriate field workable analytic methods for analyzing the performance of the system in operations.

Contributing Organizations

A number of groups participated in the project. Funding came from not only the U.S. DOE NETL but also the New York State Research Development Authority (NYSERDA). Cost share came from one of the prime partners, MI SWACO. Operating companies contributed time, effort, and sites for testing (Range Resources, BG Exco, and Norse Energy).

A number of vendors provided equipment and services to the operation. These are mentioned in the report of research.

Partnering with Universities and National Laboratories

Texas A&M GPRI served as the Principle Investigator and directed the project. Significant partnerships were created with Sam Houston State University (SHSU), Rensselear Polytechnic Institute (RPI), and Los Alamos National Laboratory (LANL). SHSU, led by Dr. Gene Theodori addressed community acceptance issues that came with the gas shale development effort in the Northeast U.S. Dr. J. Kilduff led research into advanced technology membranes and in alternate methods of flocculating solids in produced water streams. Dr. E. J. Sullivan at LANL, one of the developers of the synthetically modified zeolite catalysts for BTEX removal, led the effort to identify ways to selectively remove these carcinogenic agents from produced water streams. Reports from these agencies are included in the Appendices.

Organization and Schedule of the Program

Texas A&M GPRI managed the program. Co-sponsors formed an advisory group and field operators offered locations for the field trials. The project was organized into two budget periods that included a total of 8 major Tasks. The budget Phase 1 included Tasks 1 and 2 addressing the first the organization and schedule of the project then the technology to be developed Task 3 began the design phase of the mobile unit that was to be deployed in field trials. Staffing for the tasks was straightforward; all work performed under the supervision of the A&M staff. Key advisors from our industry co-sponsor, MI SWACO Schlumberger assisted in the design and construction of the mobile facility. A number of vendors provided specialized equipment to install in the mobile unit as it was being constructed. For each task, the DOE objectives have been identified.

Phase 2 was primarily the segment of the project where field trials were planned and performed and data analyzed.

Description of the Project: Phase 1 (Experimental Methods)

There were 4 tasks comprising Budget Period 1. This included Task 1, the Project Development Plan. Task 2 reviewed the Technology Basics and discussed a related Environmental Study, Task 3 involved designing the Pre-Treatment Work Train, and Task 4 involved Planning for Field Demonstration. Table 1 shows the first three tasks and their associated timelines. The original scope of work identified the potential problems of gaining access to sites early in 2010 and indeed the field trial portion of the project was delayed significantly because of new regulatory rules and requirements that operators were subjected to before field trials could be performed. The delay was spent in running pilot plant trials to identify optimal process design systems for the mobile laboratory.

Two organizations contributed expertise and experimental data for the project. The results of these groups were incorporated into the overall data evaluation used to select field materials for trials.

Table 1 Budget Period 1 Tasks

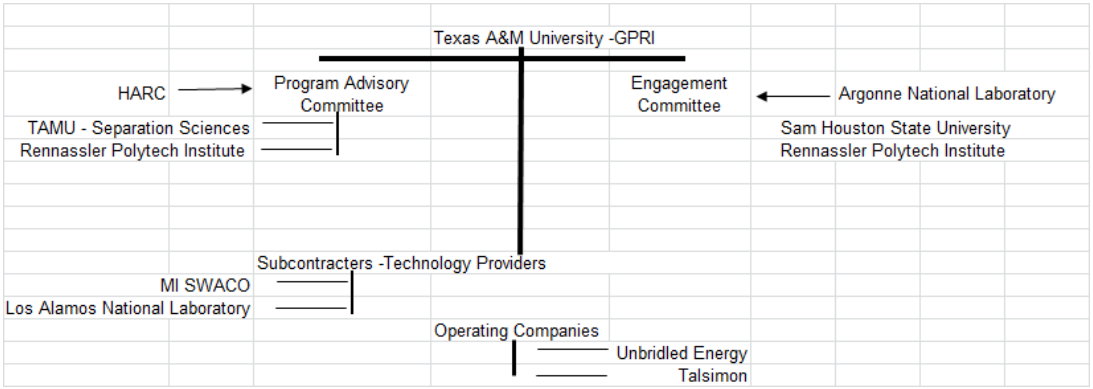
2/9/2011			Work Breakdown and Milestone Log	Milestone Log							
			Pre-Treatment								
			DOE NETL Environmental		2010				-2011		
Item Number				$3r	1st Q	2nd Q	3rd Q	4th Q	1st Q	2nd Q	3rd Q
Phase I/ Budget Period 1											
1	Task 1 –Project Management Plan					M					
1.1		Establish advisory committee									
1.2		Meet with partners									
1.3		Firm up commitments									
1.4		Seek new sponsors									
1.5		Set up communication center (coordinate with OOC)									
1.5.1			Prepare reporting schedule, model with OOC (Office of Communications								
1.5.2			Create Project Gantt Chart, detailed, with milestones, deadlines)								
1.5.3			Establish relationship with similar research program								
1.5.4			Compile similar information from other sources								
1.5.5			Identify stakeholders (local sponsors, regulatory officials)								
1.6		Hire graduate students									
1.7		Hire contractors									
2	Task 2 – Technology Basics and Environmental Study (Review).										
2.1		Meet with stakeholders (officials, construction, engineering operations) with related tasks									
2.2		Identify industry sponsor to serve on advisory committee, set strategy for field implementati									
2.3		Prepare Technology Assessment Report									
3	Task 3 – Design Pre-Treatment Work Train							M, CP			
3.1		have DOE - New York Site kickoff meeting									
3.2		Design and construct multi-function process train									
3.3		Establish IP study team for new operational practices,									
3.4		Prepare briefing documents forStakeholders									
3.5		Develop Early Models for Capital and Operating Costs									
4	Task 4 – Planning for Field Demonstration										
4.1		Prepare site,									
4.1.1.			Find contractor								
4.1.2			Identify final sites of tests								
4.1.3			Arrange construction,								
4.1.4			Prepare needed contracts								
4.1.5			Establish Matrix of performance								
4.2		Identify Regulatory Issues									
4.3		Technology transfer - Site 1									

Task 1: Project Management Plan

The project development plan for the project was straightforward. Table 2 shows the organization of the project. All work was performed at the pilot plant at Texas A&M by the GPRI Designs™ team. A report was submitted in September 2009.[1] The team stayed intact during the project with only the field sponsors having replacement organizations.

[1] Project Management Plan: Pilot Testing: Pretreatment Options to Allow Re-Use of Frac Flowback and Produced Brine for Gas Shale Resource Development, Burnett, D. B., November 2009.

Table 2 Organization of Work



Task 2: Technology Basics Review

The technology basic review was summarized in a presentation January 12, 2010 in Morgantown, WV at the NETL Headquarters. Burnett reviewed Texas A&M's 9 years of work in developing robust pre-treatment options for the use of membranes in ultra-high salinity brines such as the Marcellus Shale[2] . The Texas A&M Desalination program had shown that produced water and frac flowback brine from shale gas and tight gas well drilling operations could be treated and reused instead of tapping in to additional fresh water resources. The new DOE NETL program will demonstrate that *low cost, mobile units* can be deployed in field operations to replace the more costly and environmentally questionable practices currently being employed in field operations. The concept to be demonstrated will be that by removal of certain contaminants, a process stream can be used to provide "product water" of a specific concentration thereby recouping treatment costs. The technology thus demonstrated can be utilized for thermal processes used for desalination or membrane processes, or any other brine treatment methodology that plan to operate for extended periods in the oil field environment.

Texas A&M had previously worked with LANL on field trials of synthetically modified zeolites and so this technology was to be included in evaluations of technology suitable for incorporation in the process train of the mobile laboratory. Additionally Texas A&M had been working with a Northeast company Clearwater Inc[3]. to evaluate their technology to reduce carbonate scaling in working process streams. This technology was transferred to RPI where Kilduff and his workers developed a comprehensive evaluation program.

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2 Kickoff Meeting Presentation Pilot Testing Pre-Treatment Options …. NETL Project Number: DE-FE0000847
Burnett, D. B. Jan 2010.

[3] http://www.clearwaterinc.net/ accessed 03.28.2013 D. B. Burnett

Task 3: Design Pre-Treatment Work Train

- *Designing a Robust Field Process System*

The laboratory testing program as of December 2010 had identified the processes most appropriate for the hyper-saline flow back and produced brines encountered in Marcellus completions. In the first quarter of 2011, the final design was used to construct the process train in the mobile laboratory. Prior to selection of the laboratory's components, pilot tests were conducted to assure the performance standards would be met. Pilot tests also gave the A&M team experience in monitoring performance of the component and in selecting the most appropriate analytic test to employ in field operations.

The mobile unit incorporated a data-acquisition system that monitors flow behavior, pressures, water quality and power loads (kWh or hp) of the various pumping and treatment combinations of water pretreatment. All systems were designed to operate below 200 psi, thus reducing construction costs and lowering power costs of the low pressure pumping system. The "thoughput-gpm" depends upon the separation efficiency of the component which depends upon the composition of the raw water stream. The higher the salinity, the more energy is needed to pump brine through the membranes

Mycelx Inc. provided filtration to remove oil and grease. The filters performed successfully in pilot plant tests and were installed in the mobile laboratory.

Polymer Ventures Inc. has also provided filtration to remove oil and grease. Multiple trials in pilot plant tests have been encouraging and so the filters are included as one component in the mobile lab.

ABS Systems Inc. has provided a commercial product as an alternative to the Los Alamos product. A modified naturally occurring material designed to remove oil and grease from waste streams, we found the material to be effective and removed over 90% of the BETX in the pilot plant trials of the process system. It was included in the mobile lab process train.

Los Alamos National Laboratory tested a commercially-available filter media housing containing modified zeolite (surfactant-modified zeolite or SMZ) porous medium for use in pretreatment of frac flowback (FF) waters. The SMZ was tested previously in October 2010 in a lab-constructed configuration, and in April 2012 in the current configuration, both times for treatment of oil and gas produced water (PW). Previous tests were designed to remove benzene, toluene, ethylbenzene, and xylenes (BTEX) from PW. The current modular system is designed for field use and can be used in multiple configurations in parallel or series with standard fittings. This allows the field operator to add or subtract SMZ filters as needed to accommodate site-specific conditions, and to swap out used filters easily in a multi-unit system. This test demonstrated the use of the commercial filter housing with a simple flow modification and packed with SMZ to be used with FF source in Washington, PA. The goals of this test were: 1) to determine performance of the SMZ and filter housing with FF waters, and 2) to observe the range of backpressures encountered over a 2 gpm, 1000 gallon total volume flow test.

- *Construction of Mobile Laboratory/Water Treatment Unit*

Table 3 shows the preliminary operational plans for field trials. Prior work provided the design list of components for the mobile unit, their function and the arrangement in the overall process

train. By the time the process train was constructed, each component had been tested and vetted in the GPRI Separation Sciences Pilot Plant.

- *Membrane Selection Tests*

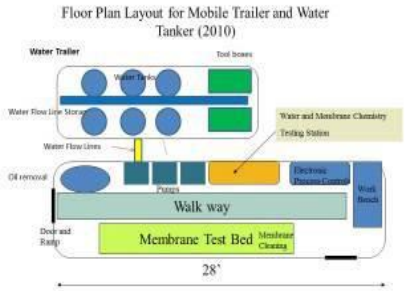
Koch ceramics were used in the mobile lab**.** This filter along with Pall hollow fiber membranes and stainless steel membranes were all tested in the field trial in the 1st Quarter. The key to success of the filters are their ability to be cleaned by back flushing and washing with chemical cleansing agents. Dow NF filters were one of the membranes chosen for mobile lab and were tested successfully in numerous pilot plant tests. Feed brine for these membrane filters must be free of dissolved solids as they are configured in a spiral wound configuration and are not amenable to back flushing or chemical cleansing. The trial also tested NF membranes from GE and from Hydranautics.

Table 3 Preliminary Operation Plans for Field Trials

Preliminary Plans for Multi-functional Pretreatment Unit Prototype Deployment to Marcellus Shale			
		DBB June 24, 2009	
Step 0			
	Identify Facility/Site Support Items		
		Covered pad for unit(s) equipped with some sort of spill control for brine spills	
		Iplace for unit	
		laboratory trailer	
		storage shed	
		Power to site (220v 3phase and transformer to provide 110v. 30 amps multiple pumps)	
		Compressed air sources (tanks or cmpressor)	
		Fresh water sources (municipal, well water, or trucked in.)	
		Telephone link (data monitoring, land line or cellular conncetions)	
		storage tanks polyethylene	
			fresh water
			frac flowback
			product water
			hypersaline waste
			solid waste storage
Step 1			
	Identify Raw water screens/bag filters etc		
		Wire mesh or 25 micron (nominal) cartridge?	
		biofilm control? (ozonation, ultraviolet, chemical?	
Step 2			
	Identify Oil removal technologies		
		Polymer Ventures	
		Mycelyx	
		LANL	
		other?	
Step 3			
	Identify Microfiltration solids removal		
		Bromley's fluidized bed system?	
		hollow fiber	
		ceramic	
		Zeewead	
		Backwash and cleaning system	
Step 4			
	Identify water softening system		
		nanofilters, cartridge wound (how many types?)	
Step 5			
	Identify RO systems		
		new Dow low pressure filters?	
		others?	
Step 6			
	Identify sensors, data monitoring etc.		
		Oil in water	
		pressure/flow	
		conductivity	
		calcium hardness	
		turbidity	
		other?	
Step 7			
	List spares, and supplies		
		standard list (Carl's toolbox, everything but the kitchen sink!)	
Step 8			
	Details of deployment, work crews, base locations etc, transport etc, local business contacts, host office names contact info etc.		

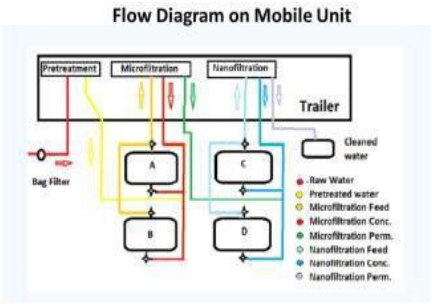
The process system was designed to provide an outlet flow capacity of 2 gm under normal operating conditions. Because membranes require high crossflow velocity, separate flow loops were required. The set of schematics below in Figure 1 show the layout of the inside of the trailer.

Figure 1 Design Layouts of Mobile Unit

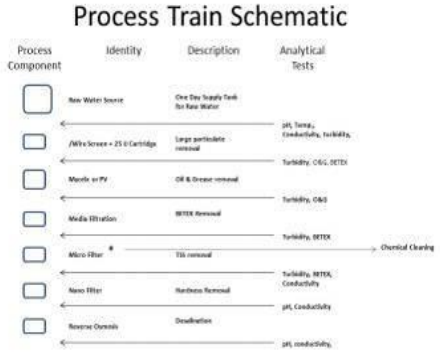


Layout of components in mobile unit.

Components of the process train.



Flow Diagram of the process train - recirculation



Analytical scheme for the components.

The team at A&M contracted for the basic mobile laboratory based on designs developed during pilot plant testing. Figure 2 shows the mobile unit on its delivery day.

Once the basic mobile unit had been delivered the GPRI team rigged it out to our specifications. All flow systems were constructed of 316 L high pressure Swagelock pipe and fittings. Two exits were designed for safety and all "wet" operations were constructed over a stainless and fiberglass platform to catch any spills. The "pump shack" was an insulated box designed so that the pumping system was outside the trailer –delivering fluids through a manifold to the flow train.

Figure 2 Mobile Unit Exterior and Interior

Top. The mobile unit was designed to be light weight and short enough to avoid needing commercial drivers. It has a retractable awning and outside LED lighting for night operations.
Left. The interior of the unit has ample bench space for instrumentation and data keeping. Overhead lockers have "safe lock" handles to prevent contents from falling out.

After the plans were in place for construction, contracts were let to build and rig out the laboratory. We decided to spend extra funds to rig the laboratory and save money by outfitting the lab ourselves. The figure below shows the bare lab being equipped with the flow line portion of the process train. The opposite side of the interior was reserved for analytical equipment, computers, and data books.

Figure 3 Mobile Unit Rig Out

The left side of the trailer was equipped with a Uni-Strut brace set to allow placement of various modules along the side.

Another feature of the "wet side" of the laboratory is the composite grate below the flow equipment. All fluids leaked from equipment makeup or changeover is collected in a tank below the trailer

The second photo in Figure 3 shows the exterior and the interior of the laboratory from when it was delivered to the installation of membrane equipment.

- *Analytical*

A comprehensive analytical test program was established in cooperation with Texas A&M TEEX Water and Wastewater Training group. Keith McLeroy (instructor at the MI SWACO Analytical Training Workshop) is working 25% of the time for the Desalination Project. By utilizing on site, real time monitoring of process train performance we increase the efficiency of the brine treatment and increase lifetimes of the components.

Task 4 Planning Field Trials

- *Partnering with Industry Sponsors*

The initial plan for the project called for collaboration with three sponsors, Norse Energy, Talisman Resources, and Chesapeake Oil and Gas. When the project began, Talisman had been sold to Statoil, Norse Energy became our New York Sponsor and Chesapeake had redirected its efforts to other gas plays. Because one of our funding sources was NYSERDA, it was important to perform a trial in New York and efforts were focused on getting approvals from both the state and DOE NETL. Since the state of New York had banned drilling in the Marcellus, an alternate plan was approved to run field trials on produced water from the Herkimer (Silurian age) formation that had similar characteristics to Marcellus brine.

Concomitantly with this effort, Range Resources approved a field trial and began work to get approval from the state of Pennsylvania to allow testing in Washington Co. BG-Exco Resources partnership also offered a site in Worthington Co. PA. that already had a state testing permit for water treatment.

- *Acquiring Permits and Approvals*

The A&M team spent significant administrative efforts to obtain all approvals necessary to perform the field trials. As described previously, all delays were overcome and the trials scheduled. Pennsylvania permitting requirements had changed in the time between approval of the Marcellus program and 4 months were spent waiting on new approval.

- *Field Operations Plans*

Field operations plans were prepared for each field trial. Each ops plan included necessary NEPA forms.

The Field Operations Plan for the field site in Chenango County, NY was provided to Norse Energy. The Texas A&M mobile laboratory, equipped with different types of pre-treatment technologies would be sited near a producing gas well from the Herkimer formation (Silurian Age). Brine analysis by A&M showed the similarity between this produced brine and the composition of brine produced from the Marcellus Shale formation underlying the Herkimer.

A similar Field Ops plan was created for the field trial in Washington Co. PA. The test was conducted during the 3th quarter of the year 2012. As in the New York trial, the specific goal of the field trial was to develop and utilize a mobile unit to demonstrate the effectiveness of

different membrane technology suitable for use with high salinity flow back brines and produced water from the Marcellus Shale.

The last Field Operations Plan described our planned activities at a field site in Worthington County, PA provided by EXCO Resources. The Texas A&M mobile laboratory, equipped with different types of pre-treatment technologies is sited near a producing gas wells operated by EXCO Resources. The same configuration as used in Field Trial 1 (New York) will be utilized again.

Description of Project: Phase 2 Field Demonstrations

Phase 2 of the project consisted of four tasks, Task 5 Mobilize Equipment to Test Site, Task 6 Operations: Performance, Monitoring, Task 7 – Analyze Performance, Task 8 – Technology Transfer and Final Report. The schedule of the field trial portion of the project is shown in Table 4.

Table 4 Schedule of Field Trials; 2011 - 2012

		Pre-Treatment DOE NETL Environmental	2011				-2012		
Item Number			1st Q	2nd Q	3rd Q	4th Q	1st Q	2nd Q	3rd Q
Phase II/ Budget Period 2									
5	**Task 5A Mobilize Equipment to Texas Site for Operational Trials**						M		
5.1		identify site							
5.2		mobilize equipment, set trial schedule							
5.3		run field trials							
5.4		Demoblize and cleanup							
5	**Task 5B Mobilize Equipment to Marcellus and Integrate with Infrastructure**								
5.1		Upgrade process system and mobile lab as required							
5.2		identify site							
5.3		Mobilize to site							
5.4		run field trials - Marcellus							
6	**Task 6 Operations: Performance, Monitoring and Demonstrations.**								
6,1		Establish monitoring schedule							
6.2		Set up internet based monitoring, Matrix of performance, data analysis							
6.3		Set up performance standards							
6.4		Create schedule of visits by sponsors							
6.5		Monitor unit operations							
6.6		Monitor A&M pilot plant units							
6.7		Prepare monitoring reports							
6.8		Prepare demonstration reports							
6.9		Plan for conclusion or for continuation of testing							
6.10		Shut down project, demobilize or phase project into next Phase							
7	**Task 7 – Analyze Performance of Pre-Treatment Systems.**								
7.1		Matrix of performance, data analysis							
7.2		Compare with standard systems							
7.3		Analyze Project							
		Conclusion of Field Testing and Analysis							
8	**Task 8 – Technology Transfer**								
8.1		Coordinate with stakeholders							
8.2		Write technical publication							
8.3		Plan wrapup of DOE project Phase 1							

Field Operations: Shakedown Trial in the Eagle Ford

A preliminary field trial was conducted in South Texas the week of February 8 through February 14, 2011 to test out equipment and logistics of moving to remote sites. The test was conducted at an actual well pad so that not only could the equipment be checked but preliminary information could be obtained on the type of cleanup that would be required for brine re-use at the location. The site was on the Cerrito Prieto Ranch in Webb Co. TX. Figure 4 shows the unit at the site.

Figure 4. Unit at Cerrito Pietro Ranch, Webb County, TX

The mobile lab was placed adjacent to a frac pond at the edge of well pad 10, 11. The unit requires a 100 amp power source –a rental unit is shown in the picture. Spares and expendables were in the box truck shown. Frac flow back brine was pumped into the lined pit by transport trucks or by flow lines (not shown). Brine is then pumped to the next frac job. We recommend such brine be filtered to remove contaminants before re-use.

Seven types of water treatment technology were tested. Oil removal, (Mycelx, Polymer Ventures, ABS) Microfilter (hollow fiber, ceramic, stainless steel), and Nanofilters (spiral wound) were the optional treatment technologies. Reverse Osmosis membranes and the chemical cleaning system were not evaluated during the trial run.

Field ops were performed in the following manner. The first test series (tests 1 and 2) were performed to measure the ability of different materials to selectively remove hydrocarbons and other petroleum components from frac pond brine.

Test 1 was conducted at a flow rate of 2gpm through the media filters. Initial frac pond brine was pumped through a sock filter (10 micron nominal), then Mycelx media filter then ABS BETEX removal. Filtrate (permeate) was collected in an oil free brine tank ("Tank 1") for subsequent micro filtration.

Test 2 repeated the first test except that a Polymer Ventures filter was substituted for the Mycelx filter.

The second test series (tests 3, 4, and 5) evaluated the effectiveness of the micro-filters to remove solids (TSS).

Test 3 evaluated TSS removal of a ceramic filter. This filter utilizes cross flow filtration at high pump rates to reject solids greater than 0.2 micron in size. Oil-free brine was pumped from Tank 1 across the filter and permeate collected in a solids free poly tank ("Tank 2") on the water trailer adjacent to the mobile

lab. Samples were taken for turbidity measurement.

Test 4 was conducted in the same manner as test 3 with the substitution of the Grave stainless steel micro-filter.

Test 5 was conducted in the same manner as tests 3 and 4 using a hollow fiber micro-filter for solids rejection.

The last test series measured the ability of the nano-filter to remove certain dissolved solids (salts) from the solids-free brine.

The field trial lasted a week. Results of the test sequences are shown in Table 1. The test sequences refer to the arrangements of the process train. The design of the system requires three sequential operations (1) oil removal (hydrocarbon) removal, (2) suspended solids removal, and (3) dissolved solids reduction (softening). Table 5 shows the analytical results of the comparison tests- all of the hydrocarbon materials (oil and grease and BETX were effectively removed. Media material worked effectively through the entire test period with no indication of fouling or allowing hydrocarbon to be produced. Table 5 serves as a summary of the performance of each of the test sequences.

Table 5 Summary of Brine Cleanup

Table 2. Summary of Brine Clean up

Draft Version March 29,2011

Sequence No.	Technology	Operating Conditions			Performance					Comments
		Feed Flow Rate, gpm	*TMP, psi*	*Average Discharge Flux, L/M/Hr*	*Analytical test*	*Material removed*	*Initial*	*Final*	*Removal Efficiency**	
	Raw Water from Pond	—	—	—	Turbidity			162	—	
1	Pre-treatment-cartridge (10 micron nominal)	2	2	—	Turbidity	Suspended solids	160	105	66%	
2	hydrocarbon removal									
	Mycelx -cartridge	2	2	—	Oil & Grease		105	100	5%	Feb. 19
	PV cartridge	2	2	—	Oil & Grease					
	ABS BETEX	2	2	—	Volatile Organics					
						Benzene	83	20.6	75%	
						Ethylbenzene	10.4	<.5	99%	
						Toluene	244	32.3	99%	
						Xylene	178	46	87%	
		Recirc. Flow Rate, gpm								
3	TSS Removal									
	Pall Ceramic	5.6	30	36	Turbidity	TSS	105	0.67	87%	19-Feb
	Graver Stainless Steel	6.4	32	35	Turbidity	TSS	105	4.8	87%	
	Pall Hollow Fiber	8.4	25	90	Turbidity	TSS	105	0.47	87%	
4	TDS Removal									
	Dow NF	4.9	150	0.6	Turbidity	TSS		1.51		
						TDS				
						conductivity	989 uS/CM	1.45 uS/CM	99%	
						chlorides	7000 mg/L	5,000 mg/L	71%	
						alkalinity	6900 mg/L	13.9 mg/L	100%	
						sulfates	50.0 mg/L	20.0 mg/L	60%	
				* Efficiency = 1- (C-final/C-initial)						

The data collected show the importance of suspended solids removal and the effectiveness of microfiltration as a process component. Further process train modifications would include an upgrade of micro filtration capability. Since the physical footprint size of hollow fiber filters was significantly smaller than stainless steel or ceramic filtration, further field trials would focus more intently of these types of filters.

Field Operations: Extended Testing in Chenango Co. NY

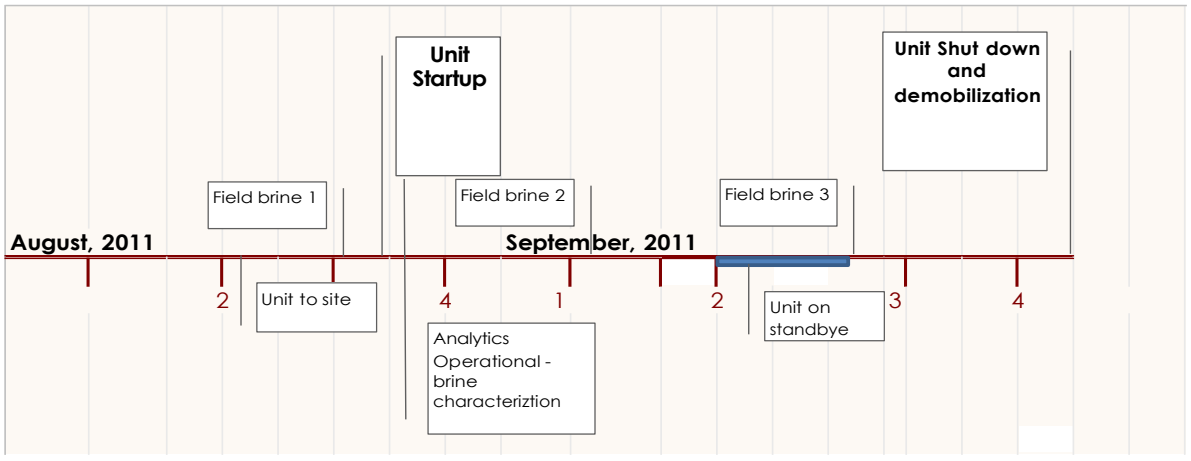
The mobile unit, with checkout and field trials complete, was moved to the Marcellus Shale for a four week duration field trial.

Figure5A shows the mobile laboratory at the New York field site. Also shown in is the environmental "apron" placed beneath the lab to catch any liquid spills.

Figure 5b shows the layout of the unit at the site. Shown (left to right) are the field brine tank, the mobile power, the laboratory, brine tanks, and the waste tank..

The field trial was conducted over a four-week period. Figure 6 shows the approximate timeline for the trial and when each of the field brines was tested. All field brines were and stored in a 100 barrel supply tank. All processed brine and waste fluids were pumped to a 100 barrel disposal tank. During the second week in September, the unit was placed in standby mode to await final approval by DOE. Figure 3 shows the timeline for the trial.

Figure 6 Trial Timeline, Norse Energy



Monitoring

The performance of each technique was measured by its separation efficiency, power consumption, and ability to withstand fouling. On site analysis of water from each step of the process train allowed real time monitoring of each component. (Figure 1 shows the measurements that made up the monitoring protocol.)

Media Filtration (Hydrocarbon Removal)

Discussion –two stages of media filtration designed to remove hydrocarbons. Step 1 consisted of oil and grease removal. Two types of oil and grease removal were tested. Mycelx[4] and Polymer Ventures[5]. Both of the materials were cartridges in standard filter housings.

Mycelx (Connie Mixon) – media filtration to remove oil and grease. Experimental results based on TEEX analytical tests showed efficacy in multiple trials. The process became a planned component in mobile lab.

Polymer Ventures (Jonathan Fabri) - media filtration to remove oil and grease. Experimental results based on TEEX analytical tests showed efficacy in multiple trials. The process became a planned component in mobile lab

ABS. A modified naturally occurring material designed to remove oil and grease from waste streams. The material was effective and removed essentially 100% of the oil and grease from produced water and over 90% of the BETX, but exhibited a tendency to produce colloidal material that increased turbidity in analytical samples.

Shown in Figure 7 shows the canisters for low pressure media filtration while the second photograph shows an image of the ABS material used for BETX removal.
.

Figure 7A Oil and Grease removal cartridges. Two types were tested. Each performed acceptably.

Figure 7B BTEX Removal. The larger containers are required to meet the requirement of 6 minutes in contact with media.

Analysis of produced brine before and after media was performed on site with advanced

4 http://www.Mycelx.com
5 http://www.PolymerVentures.com

technology equipment. Results showed reduction in TOC and in turbidity. Turbidity decrease will generally indicate retention of suspended solids although in our trials, no increase in pressure drop across the media was observed. (For a typical 300 gallon run through the media with field Brine 1 there was no discernible increase in differential pressure across the filters

Overall, the field trial was a success. Of the four field brines evaluated, three were treated with minimal problem. Over 16,000 gallons of brine were processed. Using a power cost of $0.10 per KwH, media pretreatment power use averaged $0.004 per barrel, solids removal $0.04 per barrel and brine "softening" $0.84 per barrel. Total power cost was approximately $1.00 per barrel of fluid treated. This is shown in Table 6.

Table 6 Cost of Powering Process

Samples	Date	Test Description	Duration	kw used	cost per bbl
S-62, S-63	Sept. 2	Running Dow NF (B)	3.35	0.2	$ 0.84
S-58, S-59	2-Sep	Koch U-F			$0.0275
S-84, S-85	Sept. 20	media	325 gal.	0.3	$ 0.0039
		Koch UF	63.63	2.1	$ 0.14
					$ 0.98

Field Operations: Extended Testing in Washington Co. PA

The analytical team comprising the Advanced Analytical Roundtable supported work at the Range Resources site. The group planned an organized approach to upgrading on-site analytical services for O&G operations in unconventional reservoirs such as the Marcellus and the Eagle Ford Shales. A new RPSEA research program was created for advanced analytics.

Advanced Oil Coalescer Filtration Testing

A new oil coalescer device was tested at the A&M pilot plant prior to field deployment. The device is designed to collect any significant oil carry over from field operations that might enter the brine stream being treated. Test results were positive and a unit was shipped to the field.

- *Field Operations*

Range Resources has provided a site for the second field trial of pre-treatment. The site, located in Washington Co. PA (South of Pittsburgh) was visited and water samples taken for analysis. A field plan was prepared and approved by DOE NETL and Range Resources. Testing occurred during the month of September. Figure 8A shows the mobile lab at the site.

Figure 8B shows the laboratory crew Frank Platt and Carl Vavra with Dr. Jeri Sullivan from the Los Alamos National Laboratory at the site observing the tests.

Figure 8A. Mobile laboratory set up in Washington Co. PA. The site was an active produced water storage facility with as many as 10 trucks per hour arriving and leaving with brine.

Figure 8B. Dr. E. J. Sullivan supervised the test of the updated SMZ BTEX removal system during the Washington Co. test. Frank Platt and Carl Vavra are the lab operators.

- *Micro-Filtration Performance*

Three types of micro-filtration were used and as found previously in New York trials, the Koch hollow fiber membrane was superior. Figure 9A shows inlet and outlet produced brine samples while Figure 9B shows a relative comparison of the membrane performance.

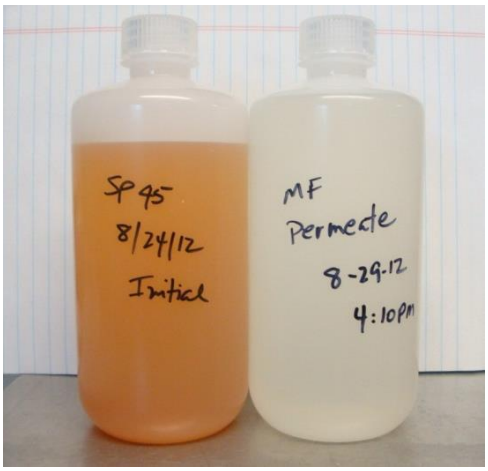


Figure 9A. Micro-Filter Performance. Photo 3 shows a sample collected during the microfilter run mid-test. Turbidity was reduced from over 100 to less than 2 with no sign of micro filter fouling.

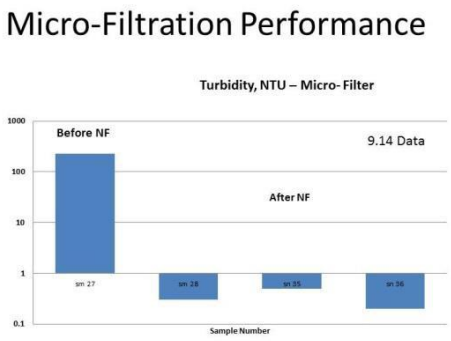


Figure 9 B Turbidity tracks suspended solids and hydrocarbon content. Micro-filtration effectively removes the contaminants that would cause formation damage if present in fracturing fluids.

Nano-Filtration Performance

Nano-filtration was used to "soften" the field brine to make it more stable and amenable for use as a make-up fluid for fracturing. This technology uses spiral wrapped membrane filters that are the same style as reverse osmosis filters but manufactured in a way that rejects a significant

amount of divalent ions in brine solutions. Both iron and sulfate ions, both problematic in frac fluid make-up brines are excluded with properly designed nano-filtration.

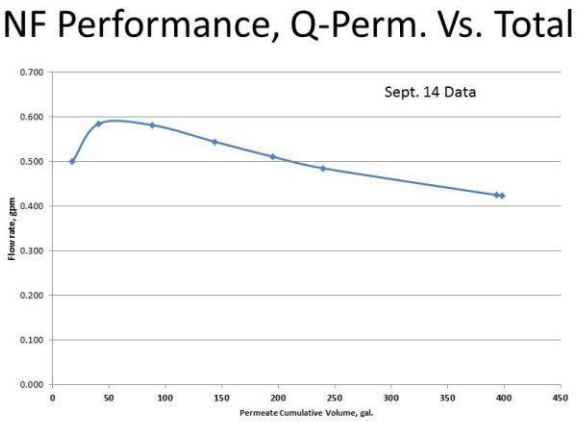
Testing at the site indicated that the ultra-high salinity brine could be treated effectively with membrane filtration. Table 7 shows the inlet and outlet iron content measured on-site in Washington Co.

Table 7 Nano-Filtration Ultra-High Salinity Brine

sample #	tds	turbidity	onductivit	toc	iron	pH	comments
SN 6	184.2	0.68	111.1		9.7	6.16	Nano Feed
SN 7	184.5	0.79	111.6		9.7	6.16	Nano permeate
SN 8	195	0.9	120.2	113	10	6.1	Nano Feed
SN 9	189.4	0.4	114.7	72.6	10.2	6.1	Nano permeate
SN 10	200.7	0.8	121.2	120	11.9	6.11	Nano Feed
SN 11	190	0.5	113.7	75.3	10	6.11	Nano permeate
SN 12A &	202	0.67	127.3	167	12.6	6.16	Nano Feed split smple
SN 13A & I	197.8	0.43	121.5	94.4	11.4	6.19	Nano Feed split smple

A second indicator of nano-filtration performance efficiency is the filtration efficiency of the component. Figure 10 shows the pressure-rate data of a nano-filtration run with brine that had been pre-treated with micro-filtration.

Figure 10 Nano-Filtration Performance



- *Benefits of the Field Trial*

Overall, the field trial was a success. The process train tested by GPRI operated successfully for over a month with few problems. The media filters performed adequately and lowered hydrocarbon content to such a value as to cause no fouling problems with downstream filters. The microfiltration membranes all functioned satisfactorily to remove suspended solids with turbidities ranging up to 500. Finally the nanofilters that were used to reduce alkalinity

performed to spec. Overall of the four field brines evaluated, three were treated with minimal problem. Over 6,000 gallons of brine were processed. Using a power cost of $0.10 per kwh, media pretreatment power use averaged $0.004 per barrel, solids removal $0.04 per barrel and brine "softening" $0.84 per barrel. Total power cost was approximately $1.00 per barrel of fluid treated.

Field Operations: Extended Testing in Worthington Co. PA

The field trial procedures and equipment were based on the successful A&M GPRI Produced Water Treatment Program in the previous Armstrong Co. PA trial and the Chenango Co. NY trial in 2011. Additionally the sponsors (the BG-Exco Partnership) requested that testing could be used to help identify key technology requirements for any commercial operations at their water storage sites in NW PA.

The operations plan for the trial was prepared and submitted to DOE NETL and to the operator in advance of testing. On August 8, 2012[6] . The Field Operations Plan described planned activities at the field site in Worthington County, PA provided by BG Exco Resources. The Texas A&M mobile laboratory, equipped with different types of pre-treatment technologies was sited near a brine containment pond used to collect frac flow back and produced waster from BG Exco partnership wells.

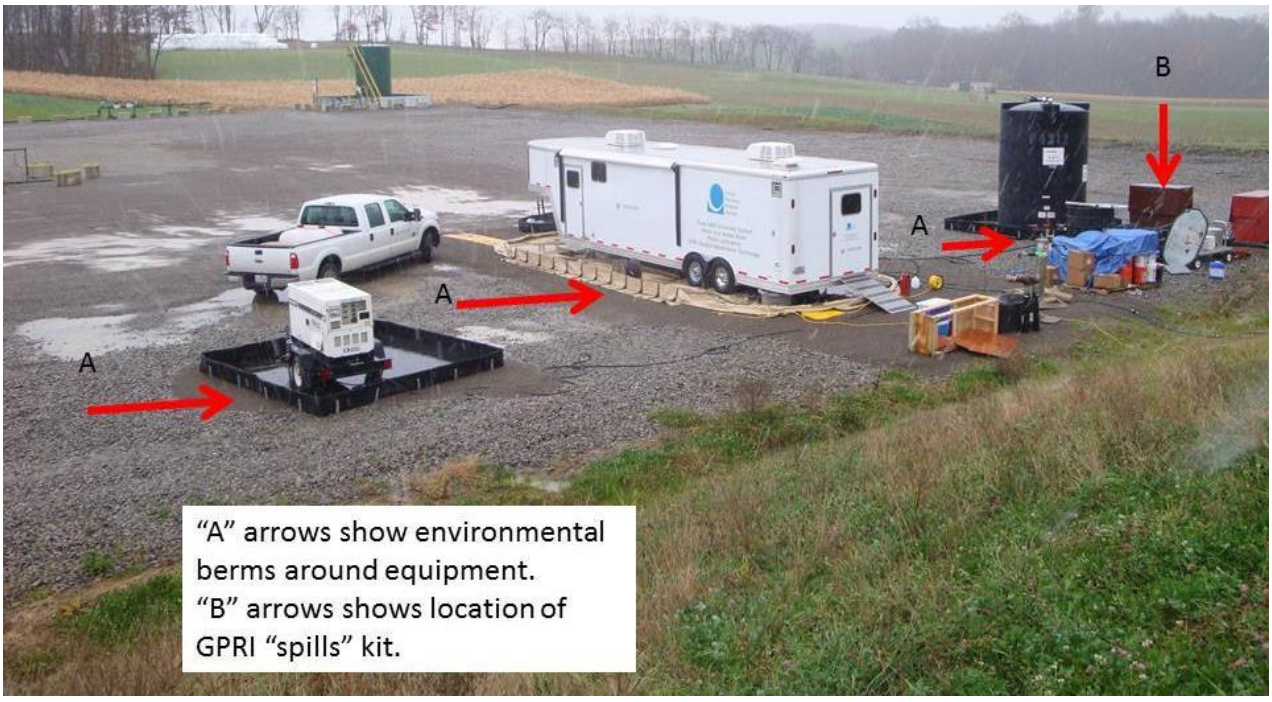


Figure 11 shows the mobile laboratory in Worthington Co. PA. The well pad was protected from spills by placement of environmental containment pads beneath the equipment. (Tropical storm "Sandy" filled them with water that had to be discharged into the frac pond.

[6] Report to DOE-NETL Pilot Testing: Pre-Treatment Options- Worthington Co. PA, Burnett, D. B., August 8, 2012

The Plan for the 2012 program as required by the U.S. DOE NETL as part of our funded project. The goal of the project was to identify a reliable and cost-effective pre-treatment methodology for use in processes employed to treat and re-use field-produced brine and fracture flow back waters. The project aimed to develop a mobile, multifunctional water treatment specifically for "pre-treatment" of field waste brine and conduct field tests of the technology. This was the fourth trial scheduled and the second test in the Marcellus Shale in Pennsylvania.

The objective of testing at this site is to evaluate what type of pre-treatment is most cost-effective water management technique for use to allow Marcellus Shale brines to be re-cycled and re-used in a beneficial manner for subsequent O&G operations.

Performance of Pre-Treatment Units and Key Findings of Technology

The project work showed conclusively that ultra-high salinity brine was not an impediment to pre-treatment and re-use of brines, either frac flowback brine or produced water. Extended duration testing with different types of brines showed that membranes were robust and could be operated for long time periods with no fouling.

In addition to the high salinity, the process system was challenged by instances of high iron content (both dissolved iron and colloidal iron) and by high bacterial counts in the raw waters, despite salinities greater than 100,000 tds. Microfilter systems that allowed for back washing and pressure pulsing were the most successful for removal of the contaminants.

The Pennsylvania field trials were not a severe test for the process system components designed for hydrocarbon removal as the brines tested were from gas wells, not condensate or oil wells. The Eagle Ford "pre-trial" was performed with water from condensate producing wells and that data validated pilot plant trials that showed effective removal of oil and grease and of BETX by the vendor materials installed in the process train.

Conclusions and Recommendations

A number of discrete filtration processes have been examined and incorporated into a singular work process flow train suitable for mobile operations in water treatment (water resource management). Field trials in four locations have provided data that can be used to estimate the relative cost and performance of this novel new pre-treatment design for brine waters destined for recycling in the oil field.

The mobile unit has been designed to monitor power loads (kWh or hp) of the various pumping and treatment combinations of water pretreatment. Pre-treatment processing operates at pressures below 500 psi, thus reducing construction costs and lowering power costs of the low pressure pumping system. The "thoughput-gpm" depends upon the separation efficiency of the component (Col. 3) which depends upon the composition of the raw water stream. The higher the salinity, the more energy is needed to pump brine through the membranes. Pumping requirements for each step of the process train are shown in Table 5.

The prototype model will be a template for evaluating the efficiency of the field unit with varying configurations. Table 6 shows the energy requirement component of the model (Energy cost represents the major expense of operating the unit.). It is seen that the total power cost to

treat the ultra-high salinity brine, remove hydrocarbons, suspended solids and alkalinity was less than $1.00 per bbl of water treated.

Overall, the field trial was a success. The process train tested by GPRI operated successfully for over a month with few problems. The media filters performed adequately and lowered hydrocarbon content to such a value as to cause no fouling problems with downstream filters. The microfiltration membranes all functioned satisfactorily to remove suspended solids with turbidities ranging up to 500. And finally the nanofilters that were used to reduce alkalinity performed to spec. Overall of the four field brines evaluated, three were treated with minimal problem. Over 6,000 gallons of brine were processed. Using a power cost of $0.10 per kWh, media pretreatment power use averaged $0.004 per barrel, solids removal $0.04 per barrel and brine "softening" $0.84 per barrel. Total power cost was approximately $1.00 per barrel of fluid treated.

Because Oil removal and solids rejection are appropriate for both thermal techniques and membrane treatment systems, work will continue to measure the effectiveness of the various pre-treatment techniques. New analytical procedures will be used to measure the effectiveness of other processes offered by commercial providers.

Acknowledgements

This work has been supported by GPRI sponsors, the U.S. DOE NET, RPSEA and the Environmentally Friendly Drilling Program (EFD). Thanks go to our field supporters Escondido Resources, Norse Energy, and Range Resources. Special thanks go to MI SWACO for their continued support of the A&M program and their insight into field operations.

APPENDIX

New York Field Trial of Ultrahigh Salinity Brine Pretreatment: Environmentally Friendly Drilling Technology for the Marcellus Shale

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c - 201

Abstract
Shale gas development relies heavily on multi-stage hydraulic fracturing to maximize the economic viability of each new well. In recent years, the industry is aiming at re-use of frac flow back brine to reduce costs and environmental impact of operations. The challenge is to identify technologies and approaches for treating the frac water that returns to the surface following a frac job (frac flowback water) for beneficial re-use in other applications, thereby conserving other local freshwater supplies. Field trials in upstate New York have been conducted to test new technology to treat brines characteristic of flow back brines from the Marcellus Shale and make them amenable for re-use in subsequent oil field operations.

Texas A&M University

Major Sponsors

Range Resources

U.S. Department of Energy National Energy Technology Laboratory

Appropriate Technology for Application in Marcellus Shale in Washington Co. PA

FINAL REPORT

Appropriate Technology for Application in Marcellus Shale in Washington Co. PA

List of Tables and Figures

Abbreviations/Acronyms

BETX	Benzene, Ethylbenzene, Toluene, Xylene
EFD	Environmentally Friendly Drilling
HARC	Houston Advanced Research Center
LANL	Los Alamos National Laboratory
MF	Micro-filter
NF	Nano-filter
NTU	Nephelometry Turbidity Units
PTTC	Petroleum Technology Transfer Council
TAMU	Texas A&M University
TEEX	Texas Engineering Extension Service
UF	Ultra-filter

Appropriate Technology for Application in Marcellus Shale in Washington Co. PA

Executive Summary

The goal of the Texas A&M GPRI DesignsTM program has long been to develop a mobile, multifunctional water treatment capability designed specifically for "pre-treatment" of field waste brine. A field trial in Washington Co. PA was conducted to show the utility of selected pretreatment methods to clean frac pond brine and make it amenable for re-use in oil field operations. Testing consisted of conducting a side-by-side comparison between new technology and that already existing in field operations.

This was the second of three (3) Field Trials that will identify Appropriate Technology for Application in the Marcellus Shale. This trial, for Range Resources, was part of the U.S. DOE NETL *Options for Water Management in the Shale*. Funding has come from the U.S. DOE NETL organization, NYSERDA, the Texas A&M University Foundation, and our industrial partner MI SWACO Schlumberger. Specifically the trial and others before it were designed to demonstrate that such techniques could be used on ultra-high salinity brines such as occurs in the Marcellus Shale.

Project Overview

Field trials utilized a mobile unit to demonstrate the effectiveness of different technology suitable for use with high salinity flow back brines and produced water. The design of the mobile unit is based on previous and current work at the Texas A&M Separation Sciences Pilot Plant.

The goals were in two categories for the field trial. First the reduction or removal of specific ions, compounds or materials from the produced water and second the optimization of treatment for reduction in media/membrane replacement and operations cost.

The A&M program was designed first to identify and second to demonstrate that membrane technology could be used to "condition" the brine characteristics of the Marcellus Shale brine at the outflow of the final stage of the process. (The target goals shown in the Table 1 (page 6) are comparative values to the results found in the Texas A&M New York Field trial in 2011). An additional aim was to obtain the approximate cost of such treatment.

Technologies Utilized in Trials

The several treatment techniques which have been found to be successful in both pilot plant and field tests have been tested to incorporate into a single multifunctional process train. Eight different components were evaluated during the trials, two types of oil and grease removal, one BTEX removal step, three micro-filters, and two different nano-filters. The performance of each technique was measured by its separation efficiency, power consumption, and ability to withstand fouling.

Results of the Trial

The process train tested by GPRI operated successfully for over a month with few problems. The media filtration to remove hydrocarbon performed satisfactorily although the site was not a true test of the various processes since there is little petroleum in the frac pond brine. Microfiltration to remove suspended solids performed well to remove solids but was difficult to keep functioning due to the presence of colloidal iron and claylike particulate in the water. We succeeded in adapting a back pulse sequence together with use of a chelating agent (1 part HAc in 1,000 parts brine). The nano filtration successfully softened the water as expected with no deterioration in flux. Total operating cost (power use only) was measured at less than 50 cents per barrel of brine treatment.

Recommendations for Treatment of Produced and Frac Flow Back Brines

The field trial was the culmination of a three year effort to identify pre-treatment methods for Marcellus Shale brine. An early trial in New York (Chenango Co.) afforded opportunities to evaluate various methods of brine treatment. The technology, commonly referred to as "pre-treatment" is an important component of the trend to re-using frac flowback brine and produced water in oil and gas drilling operations.

Our results show that pre-treatment is achievable and eminently practical. We recommend strongly that well designs for new drilling in the Marcellus take advantage of the copious quantity of brine waters available. Our recommendations come with a specific recommendation; this water to be re-used must be treated to remove certain contaminants if the subsequent well operations are to be the most productive. Our findings showed that the presence of iron, both dissolved and un-dissolved is a problem. (In addition subsequent field trials experience in Worthington Co. site in October 2012 showed the importance of avoiding or providing a means of reducing the microbial loading of the brine.)

Our overall findings lead to some specific recommendations.

1. Incorporate a corrosion inhibitor package in fracturing operations,
2. Monitor corrosion in production wells so as to prevent or minimize damage from corrosion,
3. Use biocide protection in fracturing operations.
4. Monitor produced and frac flow back brines for the presence of biological activity.
5. Defer re-use of produced brine until remedial treatments can be implemented. (Even if the flowback brine is diluted with fresh water as a makeup fluid, the risk of biological contamination in the well is too great to incur.)
6. Consider brine treatment to "soften" the produced water, subsequent brines are more readily incorporated into frac fluid packages.

Appropriate Technology for Application of Produced Water in the Marcellus Shale

Introduction

Environmental issues related to natural gas development are of mounting concern to legislators, regulatory agencies, and the general public, and threaten to undermine the economic development of this resource.

Shale gas development relies heavily on the hydraulic fracturing process in order to maximize the economic viability of each new well. The challenge is to identify technologies and approaches for treating the frac water that returns to the surface following a frac job (frac flowback water) for beneficial re-use in other applications, thereby conserving other local freshwater supplies. Texas A&M and its partners were funded to identify appropriate technology for brine treatment and to demonstrate the technology in field trials. Treatment consisted of eight (8) tasks to demonstrate frac water pre-treatment technology's ability to remove constituents from the high salinity flowback water and produced brines encountered in the Marcellus region—and accomplish this with minimal chemical usage and no adverse environmental impact.

Aim of the A&M Project

The goal of the A&M Program is to develop a mobile, multifunctional water treatment capability designed specifically for "pre-treatment" of field waste brine by conducting a side-by-side comparison between this new technology and that already existing in field operations. To accomplish this, the A&M team with its partners, tested a number of processes designed to remove contaminants from highly saline brines. Once components of a process train were identified and tested, a mobile testing laboratory was designed and constructed to allow extended duration tests to be conducted in the field.

The trial for Range Resources was to test and demonstrate that the selected technology could be used to "condition" the brine characteristics of the Marcellus Shale brine at the outflow of the final stage of the process. These target goals are comparative values to the results found in the Texas A&M New York Field trial in 2011.

Table 1 Target Values of Treatment

Characteristic/Item	**Reduction or Target Value**
Hydrocarbon Reduction	80% reduction
Turbidity	1 NTU or less
Total iron	22% reduction
Hardness Ca^{++}	50% reduction
Barium	44% reduction
Sulfate B/A	77% reduction

As the program has matured, a new goal has been identified, to seek out and utilize the most appropriate field workable analytic methods for analyzing the performance of the system in operations. Accordingly a comprehensive analytical test program was conducted to provide on-site monitoring of the process[1].

Description of the Mobile Laboratory/Water Treatment Unit

Leading up to the 2012 field trial, A&M's laboratory testing program identified the processes most appropriate for the hyper-saline flow back and produced brines encountered in Marcellus completions. In the first quarter of 2011, the final design was used to construct the process train in the mobile laboratory. Prior to selection of the laboratory's components, pilot tests were conducted to assure the performance standards would be met. Pilot tests prior to Washington Co. also gave the A&M team experience in monitoring performance of the component and in selecting the most appropriate analytic test to employ in field operations[2].

The Process Train

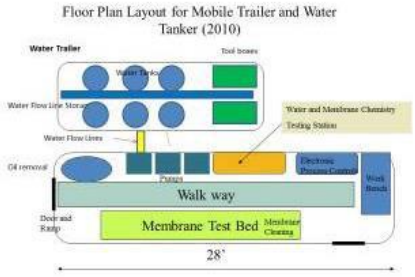
Figure 1 shows the components for the mobile unit. The floor plan layout shows how all tanks and fluid storage are located outside the laboratory but within the environmental pad (18" berm around the pad). The next graphic shows the process train components, each set in the system as a module so as to allow a "plug and play" option for different technologies. The third graphic shows the flow system for the process train. Each step of the process requires different pumping requirements. Media removal of hydrocarbon requires low pressure, low volume pumping rates. Solids removal with microfiltration requires low pressure high rate pumping. Dissolved solids removal (either nanofiltration or reverse osmosis) requires high pressure high rate pumping. The final graphic shows the analytical scheme used to monitor performance of the system. This process train served well to remove both solids (TSS) and dissolved minerals (TDS) from the ultra-high salinity brine encountered in Marcellus Shale operations. (Figure 1).

The process system was designed to provide an outlet flow capacity of 2 gpm under normal operating conditions. Because membranes require high crossflow velocity, separate flow loops were required. The set of schematics below in Figure 2 shows the layout of the inside of the trailer.

[1] Texas A&M/ GSI Environmental have launched a new research program for Advanced Analytics www.efd-aas.org

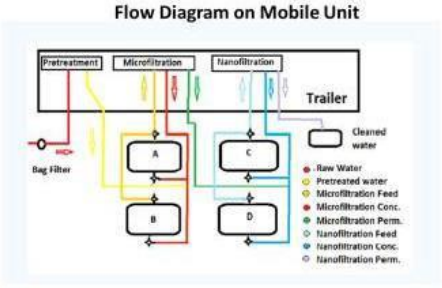
[2] Burnett, D. B., Vavra, C.A., Platt, F. A., McLeroy, L. K., Woods, R. W., New York Field Trial of Ultra-High Salinity Brine Pre-treatment: Texas A&M Environmentally Friendly Drilling Technology for the Marcellus Shale, SPE 158396 PP, SPE Annual Technical Conference and Exhibition held in San Antonio, Texas, USA, 8-10 October 2012.

Figure 1 The Mobile Unit's Design Features

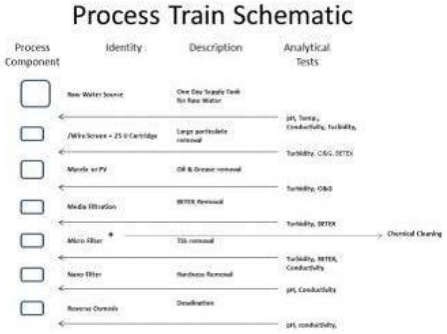


Layout of components in mobile unit.

Components of the process train.



Flow Diagram of the process train - recirculation



Analytical scheme for the components.

Analytical

A comprehensive analytical test program was established in cooperation with Texas A&M TEEX Water and Wastewater Training group. Keith McLeroy (instructor at the MI SWACO Analytical Training Workshop) formerly worked 25% of the time for the Desalination Project. By utilizing on site, real time monitoring of process train performance we increase the efficiency of the brine treatment and increase lifetimes of the components.

As a result of the effort expended on developing new analytical techniques, the expense of monitoring is lessened and the information gained is much more timely. The new GSI Environmental/Texas A&M program has been established to a) identify technologies, b) field test advanced monitoring and measurement techniques, and 3) integrate the technologies into one cost-effective program for the O&G industry.

Figure 2 Mobile Unit Interior

The interior of the membrane trailer shows media filres (in background), low pressure membranse (middle ground) and high pressure spiral wound filters (foreground). On-line monitoring sensors are also shown.

For a multi-media panoramic view of the interior of the A&M Mobile Lab, click on this web site. http://epicphotogear.com/tip/panos/

Media Filtration/Hydrocarbon Removal (Figure 1)

The mobile unit incorporated a data-acquisition system that monitors flow behavior, pressures, water quality and power loads (kWh or hp) of the various pumping and treatment combinations of water pretreatment. The media and the micro-filtration systems were designed to operate below 100 psi, thus reducing construction costs and lowering power costs of the low pressure pumping system. Nano-filtration pumping was designed for 1,000 psi. The "thoughput-gpm" depends upon the separation efficiency of the component which depends upon the composition of the raw water stream. The higher the salinity, the more energy is needed to pump brine through the membranes

Mycelx Inc.[3] provided filtration to remove oil and grease. The filters performed successfully in pilot plant tests and were installed in the mobile laboratory. Polymer Ventures Inc.[4] has also provided filtration to remove oil and grease. Multiple trials in pilot plant tests have been encouraging and so the filters are included as one component in the mobile lab.

ABS Systems Inc.[5] has provided a commercial product to remove BETX. A&M also tested a synthetically modified zeolite material obtained from the Los Alamos National Laboratory[6], a modified

[3] http://www.mycelx.com
[4] http://www.polymerventures.com
[5] http://www.pwabsorbents.com/ (transitional web link)
[6] http://www.netl.doe.gov/technologies/oil-gas/Petroleum/projects/Environmental/Produced_Water/15461.htm

naturally occurring material designed to remove oil and grease from waste streams. We found the material to be effective and removed over 90% of the BETX in the pilot plant trials of the process system. It was included in the mobile lab process train.

Membrane Selection Tests

Koch ceramics were used in the mobile lab**.** This filter along with Pall hollow fiber membranes and stainless steel membranes were all tested in both the A&M pilot plant and previous field trials (Appendix 2) The key to success of the filters are their ability to be cleaned by back flushing and washing with chemical cleansing agents.

Dow Chemical nano-filters were one of the membranes chosen for mobile lab and were tested successfully in numerous pilot plant tests. Feed brine for these membrane filters must be free of dissolved solids as they are configured in a spiral wound configuration and are not amenable to back flushing or chemical cleansing. The trial also tested membranes from GE and from Hydranautics. An experimental ultra-filter was also tested and data provided. The manufacturer has chosen not to release a commercial version at the time of this report.

The Schedule of the Program

Table 2 shows the Task Schedule for each step of the project. (A delay at the outset of the trial was an administrative stay.) Field staffing for the tasks was GPRI personnel, all trained in safety and OSHA field ops. All work performed was under the supervision of senior A&M staff.

Table 2 Test Schedule

5/28/2013	Work Breakdown and Milestone Log	Milestone Log								
	Pre-Treatment									Comments
	DOE NETL Environmental	2011				-2012				(notes, deviations)
Item Number		1st Q	2nd Q	3rd Q	4th Q	1st Q	2nd Q	3rd Q	4th Q	
Phase I/ Budget Period 1										
1	**Task 1 –Project Management Plan**		M							Marcellus Program
2	**Task 2 – Technology Basics and Environmental Study (Review).**									
3	**Task 3 – Design Pre-Treatment Work Train**							M, CP		
4	**Task 4 – Planning for Field Demonstration**									
4.1	Prepare site,									
4.1.1	Find contractor									
4.1.2	Identify final sites of tests									
4.1.3	Arrange construction,									
4.1.4	Prepare needed contracts									
4.1.5	Establish Matrix of performance									
4.2	Identify Regulatory Issues									Washington Range Resources Trial
4.3	PA State Permits - Washington Site									
Phase II/ Budget Period 2										
5	**Task 5A Mobilize Equipment to Washington Co. Site for Operational Trials**					M				
5.1	identify site support services requirements									
5.2	Set up performance standards									
5.3	Create schedule of visits by sponsors									
5.4	Establish monitoring schedule									
5.5	Set up internet based monitoring, Matrix of performance, data analysis									
6	**Task 6 Operations: Performance, Monitoring and Demonstrations.**									
6.1	Monitor unit operations									
6.2	Monitor A&M pilot plant units									
6.3	Prepare monitoring reports									
6.4	Prepare demonstration reports									
6.5	Plan for conclusion or for continuation of testing									
6.60	Shut down project, demobilize or phase project into next Phase									
7	**Task 7 – Analyze Performance of Pre-Treatment Systems.**									Wrapup
7.1	Matrix of performance, data analysis									
7.2	Compare with standard systems									
7.3	Analyze Project									
	Conclusion of Field Testing and Analysis									
8	**Task 8 – Technology Transfer**									
8.1	Coordinate with stakeholders									
8.2	Write technical publication									
8.3	Plan wrapup of DOE project Phase 1									

Description of the Field Trial

Location of Site

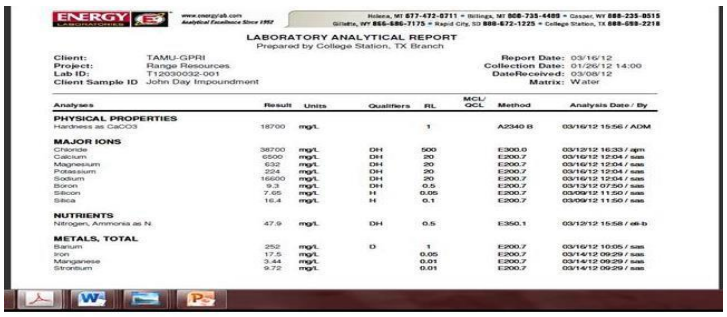
The mobile laboratory was located next to a large produced water impoundment in Washington Co. PA. Field brine was gravity fed to a 1,000 gallon supply tank adjacent to the lab. All facilities were placed on environmental pads to prevent salt water spills.

Figure 3. Mobile laboratory set up in Washington Co. PA. The site was an active produced water storage facility with as many as 10 trucks per hour arriving with brine.

Figure 4. Dr. E. J. Sullivan supervised the test of the updated SMZ BTEX removal system during the Washington Co. test. Frank Platt and Carl Vavra are the lab operators.

Analyses Brine

The brine analysis of the Washington Co. site, performed by A&M was provided to Range Resources, the operator of the site. Table 3 shows that recent compositional analysis.



LABORATORY ANALYTICAL REPORT
Prepared by College Station, TX Branch

Client: TAMU-GPRI
Project: Range Resources
Lab ID: T12030032-001
Client Sample ID: John Day Impoundment

Report Date: 03/16/12
Collection Date: 01/26/12 14:00
DateReceived: 03/08/12
Matrix: Water

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
PHYSICAL PROPERTIES							
Hardness as CaCO3	18700	mg/L		1		A2340 B	03/16/12 15:56 / ADM
MAJOR IONS							
Chloride	36700	mg/L	DH	500		E300.0	03/12/12 16:33 / apm
Calcium	6500	mg/L	DH	20		E200.7	03/16/12 12:04 / sas
Magnesium	632	mg/L	DH	20		E200.7	03/16/12 12:04 / sas
Potassium	224	mg/L	DH	20		E200.7	03/16/12 12:04 / sas
Sodium	16600	mg/L	DH	20		E200.7	03/16/12 12:04 / sas
Boron	9.3	mg/L	DH	0.5		E200.7	03/13/12 07:50 / sas
Silicon	7.65	mg/L	H	0.05		E200.7	03/09/12 11:50 / sas
Silica	16.4	mg/L	H	0.1		E200.7	03/09/12 11:50 / sas
NUTRIENTS							
Nitrogen, Ammonia as N	47.9	mg/L	DH	0.5		E350.1	03/13/12 15:58 / ak-b
METALS, TOTAL							
Barium	252	mg/L	D	1		E200.7	03/16/12 10:05 / sas
Iron	17.5	mg/L		0.05		E200.7	03/14/12 09:29 / sas
Manganese	3.44	mg/L		0.01		E200.7	03/14/12 09:29 / sas
Strontium	9.72	mg/L		0.01		E200.7	03/14/12 09:29 / sas

Laboratory Analytical Test Results: Range Resources

Before mobilizing to the Washington Co. site, the GPRI team took samples from the two most likely candidates of treatment by Range Resources. Detailed analytical report is contained blow.

Chlorides at less than 40,000 mg/L is not especially high but both the total hardness and the

organics in the brine indicated that the brine's quality would be problematic for re-use as a frac

fluid without treatment. Additionally because the brine pond was aerated (to prevent septic conditions), soluble iron was oxidized to iron^{+3}, an insoluble colloid. This material hampered filter efficiency. Figure xxx shows the brine impoundment pond.

Figure 5 shows a large brine impoundment in Washington Co. PA. By air sparging the pond, the company kept biological activity to a low level.

While not available at the outset of the A&M field trial, it was necessary to get estimates of biological activity in the pond because of the detrimental effect of organic bacteria as plugging or fouling agents. Table 3 shows a bacterial analysis performed during the A&M trial to test the performance of the experimental ultra-filter. Further descriptive information is available in the Results of Testing Section.

Table 3 Brine and Biological Materials Analysis

ENVIRONMENTAL SERVICE LABORATORIES, INC.

1803 Philadelphia St.
Indiana, PA 15701
P: (724) 463-TEST
F: (724) 465-4209
PADEP: 32-00382

1276 Bentleyville Rd.
Van Voorhis, PA 15366
P: (724) 258-TEST
F: (724) 258-8376
PADEP: 63-04247

1200 River Avenue
Williamsport, PA 17701
P: (570) 321-9002
F: (570) 321-1957
PADEP: 41-04880

Texas A & M Petroleum Engineering
3116 TAMU
College Station, TX 77843

Reported: 10/05/2012 15:28

Lab Sample ID#: 2091770-01
Sample Type: Water
Sample Source: Grab
Sampler: Client
Client Sample ID: Feed Water 0925

Sample Date: 09/25/2012 15:00
Receipt Date: 09/26/2012 08:35

Analyte	Sample Result	Units	Data Qualifier	RL	Method	Analyst/ Certification	Analysis Date/Time
General Chemistry							
Biochemical Oxygen Demand	213.6	mg/L		2.0	SM5210B	LMP/S	09/26 13:45
Microbiology							
E. Coli	ND	MPN/100 mL		1	SM9223B	CJB/S	09/26 09:10
Total Coliform	ND	MPN/100 mL		1	SM9223B	CJB/S	09/26 09:10

(A copy of the Analysis is contained on the A&M Range Resources web site[7].) Results show low biological activity which indicates that pond maintenance eliminated biological activity as a problem of concern.

Procedures

The GPRI Mobile Laboratory Field ops were performed in the following manner. The first test series (tests 1 and 2) were performed to measure the ability of different materials to selectively remove hydrocarbons and other petroleum components from frac pond brine.

Test 1 was conducted at a flow rate of 2gpm through the media filters. Initial frac pond brine was pumped through a sock filter (10 micron nominal), and then Mycelx media filter then ABS BETX removal. Filtrate (permeate) was collected in an oil free brine tank ("Tank 1") for subsequent micro filtration.

Test 2 repeated the first test except that a Polymer Ventures filter was substituted for the Mycelx filter.

The second test series (tests 3, 4, and 5) evaluated the effectiveness of the micro-filters to remove solids (TSS).

Test 3 evaluated TSS removal of a ceramic filter. This filter utilizes cross flow filtration at high pump rates to reject solids greater than 0.2 micron in size. Oil-free brine was pumped from Tank 1 across the filter and permeate collected in a solids free poly tank ("Tank 2") on the water trailer adjacent to the mobile laboratory. Samples were taken for turbidity measurement.

Test 4 was conducted in the same manner as test 3 with the substitution of the Grave stainless steel micro-filter.

Test 5 was conducted in the same manner as tests 3 and 4 using a hollow fiber micro-filter for solids rejection.

The last test series measured the ability of the nano-filter to remove certain dissolved solids (salts) from the solids-free brine.

Field Trial Results and Data

The process train was designed to sequentially remove (1) large particulates such as sediments, (2) oil and grease (entrained hydrocarbons), (3) BETX, (4) small suspended solids, and (5) dissolved multivalent ions. Analytic tests were designed to measure the relative performance of each of the sequential steps.

Guard filter Pre-treatment

Raw brine from the frac flow back pond was pumped first through a screen filter and a 10 micron (nominal) cartridge filter to remove large particulate material step (1). This "guard" filter is used as a precaution step to minimize any depth solids plugging of the media filters just downstream.

[7] https://sites.google.com/site/amrangeresourcesfieldtrial/home

The brine was then pumped directly through the media filters at a flow rate of 2 gpm (step 2).

Oil and BETX Removal

Media filters were sized (bulk volume) to allow specified residence time to maximize oil removal. Three media materials were evaluated. Samples were taken for analysis of oil content. Two materials are known to remove oil and grease, filters from Polymer Ventures, and cartridges from Mycelx Inc. and material (ABS Services) were evaluated in separate steps. Table 4 shows results. After sufficient oil free brine was collected, a separate pumping system directed the brine through the next step, microfiltration.

Table 4 Media Pretreatment of Brine

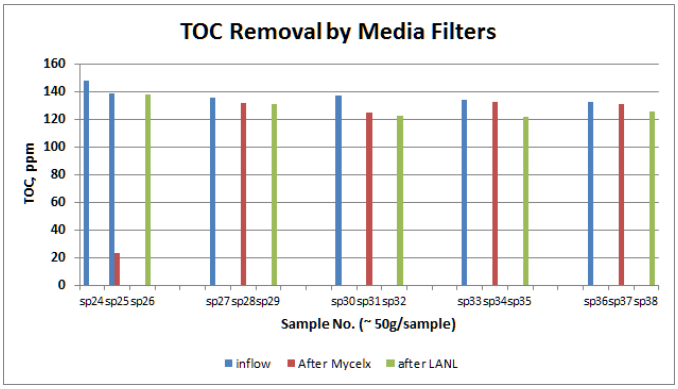
date and time	sample #	tds	turbidity	onductivit	toc	iron	pH	comments
8/23/2012 16:35	sp42	123.1	118	216.1	155			initial
8/23/2012 16:36	sp43	122.2	79.4	218.5	131			after mycelex
8/23/2012 16:37	sp44	124.8	59.9	221	115			after abs
8/24/2012 10:30	sp45	123.3	129	216.7	134			initial
8/24/2012 10:31	sp46	119.9	80.4	211.6	129			after mycelex
8/24/2012 10:32	sp47	120.4	58.7	212.7	116			after abs
8/24/2012 12:30	sp48	118.8	107	210.4	140			inlet to media
8/24/2012 12:31	sp49	120.9	74.9	213.8	131			after mycelex
8/24/2012 12:32	sp50	120.2	54.6	211.8	127			outlet abs
8/24/2012	sp51	194.3	147	119.1	118			inlet initial
8/24/2012 15:36	sp52	193.4	180	119.8	125			after mycelex
8/24/2012 15:37	sp53	190.8	131	117.4	122			after abs
8/27/2012 11:45	sp54	206.8	122	119.1	116			inlet initial
8/24/2012 15:36	sp55	193.4	180	119.8	125			after mycelex
8/24/2012 15:37	sp56	190.8	131	117.4	122			after abs
8/28/2012 9:06	sp57	121	163	205.6	120	26.9		inlet to media
8/28/2012 9:06	sp58	118.5	85.1	202.3	106			after mycelex
8/28/2012	sp59	119.7	68.9	204.3	95.7			after abs

The data show by comparison of before and after values of TOC that the hydrocarbon removal was noticeable—approximately 30% reduction in value. Reduction in values of turbidity was

also noticeable. Since these media are not designed to be depth filters to remove suspended solids, this is acceptable and actually preferable since plugging would result if the media were blocked by fouling suspended solids.

Special BETX removal media were tested incorporating material from ABS and a synthetic SMZ from Los Alamos National Laboratory (LANL). Analytical tests were performed on brines passing through the SMZ and analyzed for BETX and non-purgable organics (or total organic carbon). The results are shown in Figure 6.

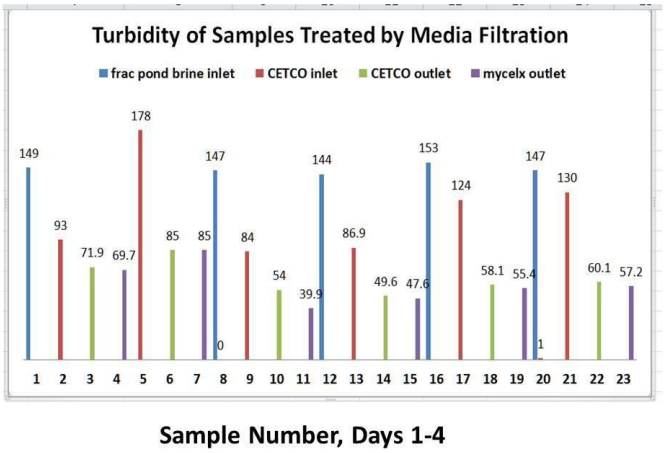
Figure 6. TOC Removal by Organics



Media Filtration and Turbidity Change

The GPRI Designs[tm] separation train uses media filtration as one of the pre-treatment steps in its process. While not an optimal solution (because these materials are "consumables"), certain types of media are effective in removing oil and grease and BETX hydrocarbons. Such media materials should not work as solids removal filters elsewise filter lifetimes are significantly reduced. The previous chart of turbidity readings taken and the following chart show readings during pre-treatment with three types of hydrocarbon removal technologies. Results show only modest removal. It is therefore necessary to design additional filtration to remove suspended solids (TSS) prior to membrane treatment to lower salinity.

Figure 7 Turbidity of Samples



Media Filtration to Remove BETX

Removing the presence of BETX from brine waters is important so that such materials are not released into the atmosphere from open ponds. (Such materials are precursors to NOx and ozone presence in air.) In addition, such materials promote biological growth. A typical sample from

the process train allows measurement of a number of contaminants, it is the goal of the A&M effort to identify then incorporate more relevant on-line testing of the fluids in the process train.

In water treatment, the primary cause of field failure is inadequate design of solids removal. The key to successful adoption of micro-filtration for solids removal lies in the design of the process train that avoids filter fouling. One feature of the A&M system is the use of micro-filtration to remove suspended solids from the brine stream. The A&M work is based on Canadian research and early commercial systems by Osmonics for municipal water treatment.[8]

Texas A&M began a program in the early 2000s to develop commercial process trains. By eliminating the conventional flocculation, precipitation, and filtration step, the process train provided a more compact system and one that uses fewer chemicals. The system being trialed in the Marcellus Shale has been tested for over 5 years in the pilot plant and in earlier trials.

Micro porous membranes are designed to retain all particles above their pore size ratings, while a asymmetric membrane is characterized by a thin skin on the surface of the membrane, rejection occurs only at the surface, and retained particles above the nominal molecular weight cut-off (MWCO) do not enter the main body of the membrane MWCO is the ability of a membrane to reject the species of certain molecular weight measured as Daltons.

Spiral wound and hollow fiber MF membranes are made of polymeric materials, for the most part asymmetric and a list of commonly used polymers includes Teflon (PTFE), polyvinylidene fluoride (PVDF), cellulose acetate, polysulfone, nylon and polycarbonate. Non-polymeric submicron membranes manufactured from durable materials such as ceramics and metallic are also used for MF separation. UF membranes provide a more complete rejection of materials, including some high molecular materials such as soluble, high molecular weight synthetic materials UF membranes are typically asymmetrical polymeric membranes like the MF membranes.

The A&M system uses UFs that can be reverse washed to reduce fouling. Best results were found with pressurized hollow fiber, ceramic, and a stainless steel. The field trials offer a way to differentiate the effectiveness of the alternatives therefore all three types were employed in the trial, ceramic, stainless steel, and capillary hollow fiber.

The system monitors filtration rate as a function of throughput (elapsed time). The data acquisition recorded turbidity (NTU) upstream and downstream of the filters. Finally the output flow rate was recorded at periodic intervals.

Advanced Oil Coalescer Filtration Testing

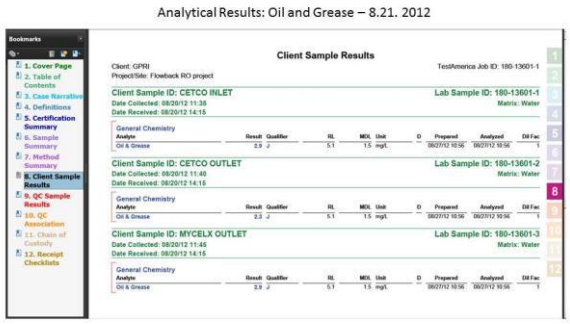
A new oil coalescer device from CETCO Energy Services[9] was tested at the A&M pilot plant prior to field deployment. The device is designed to collect any significant oil carry over from field operations that might enter the brine stream being treated. Test results were positive and a

[8] http://connection.ebscohost.com/tag/OSMONICS%2BInc

[9] http://www.cetcoenergyservices.com/

unit was shipped to the field. Testing in the field showed that the device was effective in reducing hydrocarbon content of the raw water being introduced into the process train. Figure 6 shows analytical results of the field trial of the oil coalescer.

Figure 8 Oil and Grease Removal by Coalescer



Analytical results for the CETCO oil coalescer are shown in the accompanying figure. The device performed well as a pre-treatment option in pilot plant trials and was subsequently taken to Washington Co. for the field trial.

Suspended Solids Removal

Types of Micro-Filtration Filters Evaluated

Three types of micro-filtration were used and as found previously in New York trials, the Koch hollow fiber membrane was superior.

In previous field trials, three types of micro-filters were tested in the process train, (a) ceramic, (b) stainless steel, and (3) hollow fiber filters. (These filters can be backwashed and cleaned easily, making them the best candidates for TSS removal.) However for the Washington Co. test, our process train was equipped with hollow fiber micro-filters from Koch Industries. This selection was made because of the superior TSS rejection and relatively high flux rate afforded by this configuration.

Chelation/pH Adjustment for Colloidal Iron

Colloidal iron was readily removed from the brine however the concentration of iron+2 was sufficiently high so that the resulting brines were only temporarily solids-free. As the iron oxidized, the solid colloidal iron reappeared.

To minimize colloidal iron fallout, the raw brine was treated with dilute acetic acid at a ratio of 1:1000. The lower pH created a much easier filtration operation. Figure 9 shows effects of chelation.

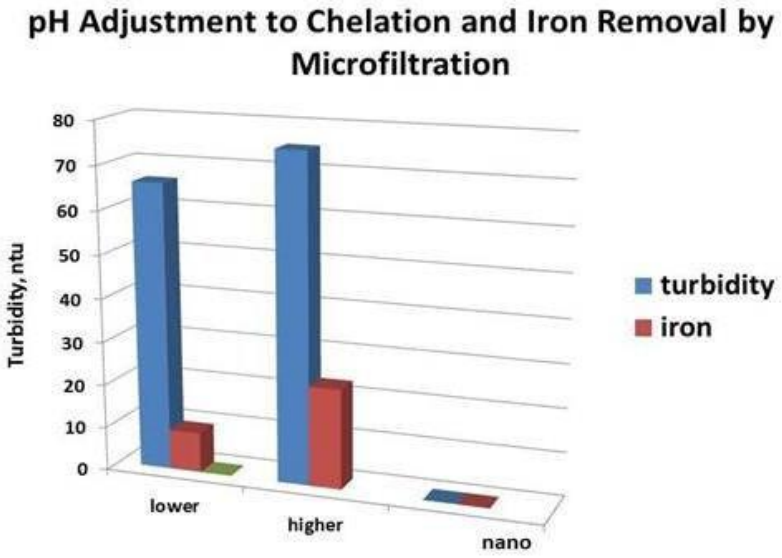


Figure 9 Adjustment for Chelation

In our Range Resources testing, we set the practice of taking the "fresh" micro-filter brine and subjecting it to nano-filtration to remove dissolved metals including $Iron^{+2}$.

Performance of Micro-Filters

Figure 10 shows the analytical results of the comparison tests of before and after micro filter tests. The "before" samples had oil and grease and BETX removed by media filtration. Since this step in the process train has been designed to remove suspended, the value for turbidity (NTU) is the important piece of data in the Table. The "before" sample (SM 27) had a NTU value of 277 while outlet samples (SM 28,29,30) had a NTU value less than 1. A second significant observation that can be made from the data is the consistency of the performance of the micro-filter over an extended time period.

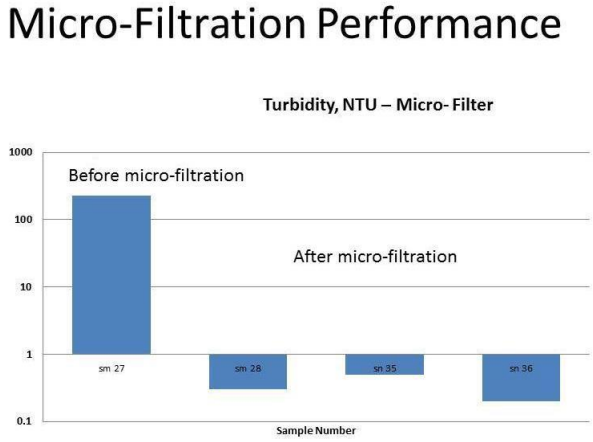


Figure 10 Micro-Filter Data

Permeate Rate vs Time

As mentioned, the colloidal iron was readily removed from the brine by the microfiltration but Problems were encountered with deterioration in flux of the filter.

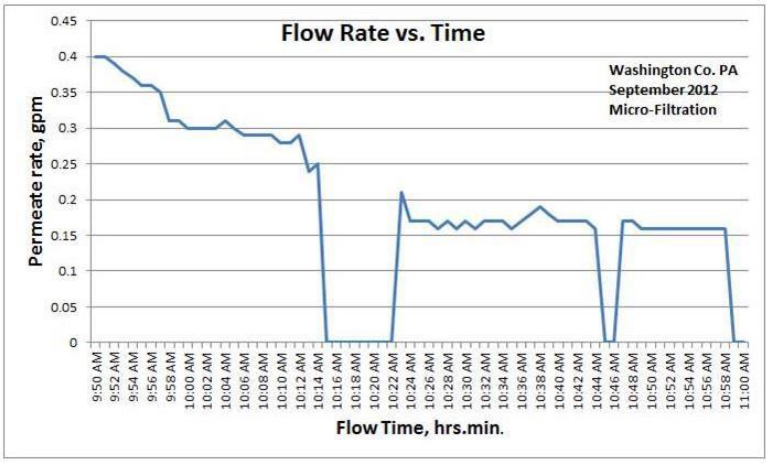


Figure 11 microfilter performance

Commercial Systems Offering Micro-Filtration Systems for TSS Removal

Finally Koch Industries has just offered commercial hollow fiber micro-filter units that have recently performed well in field applications. A&M tested these filters for the Range Resources trial (and will continue trials for the EFD-TIP program in 2013). Figure 12 shows brine samples from inlet and the outlet of a Koch micro-filter during one typical day's run.

Figure 12 Micro-Filtration Samples

Effectiveness of Koch micro-filter in removing suspended solids including colloidal iron.

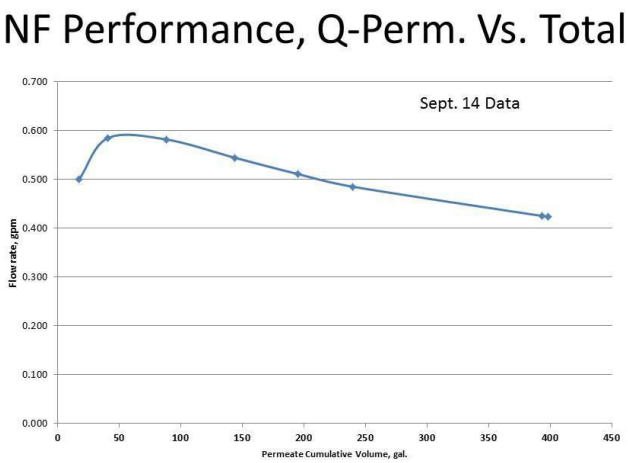
Nano-Filter Membrane Treatment

Nanofiltration (NF) is a cross-flow filtration technology which ranges somewhere between ultrafiltration (UF) and reverse osmosis (RO). The nominal pore size of the membrane is typically about 1 nanometer. Nanofilter membranes are typically rated by molecular weight cut-off (MWCO) rather than nominal pore size. The MWCO is typically less than 1000 atomic mass units (daltons). The trans-membrane pressure (pressure drop across the membrane) required is lower (up to 300 psi) than the one used for RO, reducing the operating cost significantly. Typically, NF membranes are still subject to scaling and fouling and the difficulty of using nano-filtration in the oil field is the fouling issue.

A&M's multi-step water treatment avoids the fouling problem so that the technique can be used in high salinity brines to reduce salinity and selectively remove certain divalent substances, such as sulfates and heavy metals. Flow testing measures the ability of the membrane to perform for extended periods. The chart in Figure 4 shows the flux rate of Hydranautics filter during one morning's run. The observed flow reduction was approximately 5%. Such reduction is typical and can be recovered by flushing with clean brine.

The Washington Co., site allowed the testing of nano0filtration to reduce the dissolved ions concentration in the ultra-high salinity produced water from the Marcellus Shale wells. Performance of nano-filtration was measured by the filter efficiency (how much of the brine could be treated), the pressure of the treatment, and the relative change in concentration of the dissolved ions in the before and after brines.

Figure 13 Nano Filter Performance.



The nano-filtration step is designed to reduce the ionic content of key divalent ions such as iron and sulfate. Permeate solutions are designed to be stable because of the lower ionic strength. In the case of the Worthington Co. tests, the nano-filtration was not effective. However in previous field trials, our results were more favorable as shown in Table 5. A comparison of before and after dissolved ion removal in an early trial in New York shows effective softening. Those field results were not repeated in Pennsylvania. A review of test procedures indicated that the nano-

filter was operated at a pressure below nominal and thus was less efficient. Further testing in 2013 is planned.

Table 5 Dissolved Ion Removal by Nano Filtration

		Raw Feed	Permeate	Comments
Samples	**Analyte**			
SN7, SN8	Sulfate	1025	92	Trial 1 Dow N-245 (A)
"	Chlorides	186,500	150,000	Trial 1 Dow N-245 (A)
"	Hardness	67,200	51,600	Trial 1 Dow N-245 (A)
SN60, SN 6	Iron (Fe)	183	103	Trial 1 Dow N-245 (A)
S-60, S-61	Barium - B	183	103	Trial 1 Dow N-245 (A)
SN1, SN2	Iron (Fe)	20.5	18.5	Trial 3 - Hydranautics NF
SN3, SN4	"	21.4	18.6	"
SN5, SN6	"	22	19.1	"
SN7, SN8	"	20.2	17.8	"

Conclusions and Recommendations

Overall, the field trial was a success. The process train tested by GPRI operated successfully for over a month with few problems. The media filters performed adequately and lowered hydrocarbon content to such a value as to cause no fouling problems with downstream filters. The microfiltration membranes all functioned satisfactorily to remove suspended solids with turbidities ranging up to 500. The filters required frequent back washing however because of the colloidal iron content in the brine. Further testing will be required to find the proper combination of micro-filters and cleaning aids for this specific type of brine.

Brine softening with the nano-filter used to reduce alkalinity was satisfactory. There was significant reduction in scaling material in the filtered brine and subsequent dilution to use in fracturing should have no problems with incompatibility.

The cost of pre-treatment can be estimated by observing the energy required to pump brine through the system. Based on a power cost of $.10 per kWh and using averages of three A&M field trials of ultra-high salinity brine, media pretreatment power usage averaged $0.004 per barrel, solids removal $.04 per barrel and brine “softening” $.84 per barrel. Total power cost was approximately $1.00 per barrel of fluid treated.

Table 6 Cost of Powering Process

Samples	Date	Test Description	Duration	kw used	cost per bbl
S-62, S-63	Sept. 2	Running Dow NF (B)	3.35	0.2	$ 0.84
S-58, S-59	2-Sep	Koch U-F			$0.0275
S-84, S-85	Sept. 20	media	325 gal.	0.3	$ 0.0039
		Koch UF	63.63	2.1	$ 0.14
					$ 0.98

Acknowledgements

Texas A&M has several partners who both sponsored and provided equipment and services to the development of the mobile unit. These partners assisted in the trial and contributed to its success, notably MI SWACO Schlumberger, Texas A&M EEI (Energy Engineering Institute), TEES (Texas Engineering Experiment Station), TEEX (Texas A&M Engineering Extension Service), and the EFD (Environmentally Friendly Drilling) program at the Houston Advanced Research Center (HARC). Dow Filmtec, Hydranautics, Koch Filters, Graver, and Pall (all filters) and ABS Systems Mycelx, and Polymer Ventures (media filtration) all provided products for testing. The project allowed for the identification and utilization of new and advanced analytic techniques suitable for field application. Three companies field services, GIS Environmental, INFICON, and Hach Chemicals who provided analytical services. Duke University assisted with sampling and performed analysis of radio-nucleotides. Colgate University helped with providing local service and support.

Appendices

Claypool Water Analysis
Microbiological Report
SPE 158396PP Burnett, et al (abstract)

Claypool Water Analysis Report

Sample Data from Range Resources		3/1/12	
Analyte	**Result, units**	**John Day Impoundment**	**Weimer Produced Water**
Physical properties			
pH	6.89	7.04	
TOC	mg/L	102	98.2
oil and grease	mg/L	35	20.2
Hardness as CaCO3	mg/L	18,700	65,800
Major Ions			
Chloride	mg/L	38,700	120,000
Calcium	mg/L	6,500	23,100
Magnesium	mg/L	632	2,180
Potassium	mg/L	224	355
Sodium	mg/L	16,600	44,800
Sulfate	mg/L	89	79
Sulfite	mg/L	1	1
Boron	mg/L	9	18
Silicon	mg/L	8	9
Silica	mg/L	16	19
Nutrients			
Nitrogen as Ammonia	mg/L	48	140
Metals			
Barium	mg/L	252	322
iron	mg/L	17.5	97.1
Manganese	mg/L	3	7
Strontium	mg/L	9.7	9.88

New York Field Trial of Ultra-High Salinity Brine Pre-treatment: Texas A&M Environmentally Friendly Drilling Technology for the Marcellus Shale

Burnett, D. B., Vavra, C.A., Platt, F. A., McLeroy, L. K., Woods, R. W., Texas A&M University

Abstract

Shale gas development relies heavily on multi-stage hydraulic fracturing to maximize the economic viability of each new well. In recent years, the industry is aiming at re-use of frac flow back brine to reduce costs and environmental impact of operations. The challenge is to identify technologies and approaches for treating the frac water that returns to the surface following a frac job (frac flowback water) for beneficial re-use in other applications, thereby conserving other local freshwater supplies. Field trials in upstate New York have been conducted to test new technology to treat brines characteristic of flow back brines from the Marcellus Shale and make them amenable for re-use is subsequent oil field operations.

This report describes the field trial in Chenango County conducted by the Texas A&M Desalination Program. The aim of the field trial was to develop and utilize a mobile unit to demonstrate the effectiveness of different membrane technology suitable for use with high salinity flow back brines and produced water from the Herkimer formation the brines deemed the equivalent of Marcellus Shale brine.

The several treatment techniques which have been found to be successful in both pilot plant and field tests have been tested to incorporate into a single multifunctional process train. Eight different components were evaluated during the trials, two types of oil and grease removal, one BTEX removal step, three micro-filters, and two different nanofilters. The performance of each technique was measured by its separation efficiency, power consumption, and ability to withstand fouling Overall, the field trial was a success. Of the four field brines evaluated, three were treated with minimal problem. Over 6,000 gallons of brine were processed. Total power cost was approximately $1.00 per barrel of fluid treated.

Texas A&M University

Major Sponsors

BG Exco Partnership

U.S. Department of Energy National Energy Technology Laboratory

Appropriate Technology for Application in Marcellus Shale in Worthington Co. PA

FINAL REPORT

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List of Tables and Figures

Abbreviations/Acronyms

BETX	Benzene, Ethylbenzene, Toluene, Xylene
EFD	Environmentally Friendly Drilling
HARC	Houston Advanced Research Center
LANL	Los Alamos National Laboratory
MF	Micro-filter
NF	Nano-filter
NTU	Nephelometry Turbidity Units
PTTC	Petroleum Technology Transfer Council
TAMU	Texas A&M University
TEEX	Texas Engineering Extension Service
UF	Ultra-filter

Appropriate Technology for Application in Marcellus Shale in Worthington Co. PA

Executive Summary

The goal of the Texas A&M GPRI Designs™ program has long been to develop a mobile, multifunctional water treatment capability designed specifically for "pre-treatment" of field waste brine. The aim of the extended duration trial for the BG Exco Partnership was to show the utility of selected pretreatment methods to clean frac pond brine and make it amenable for re-use in oil field operations. Specifically the trial and others before it were designed to demonstrate that such techniques could be used on ultra-high salinity brines such as occurs in the Marcellus Shale. Testing consisted of conducting a side-by-side comparison between this new technology and that already existing in field operations

Project Overview

Field trials utilized a mobile unit to demonstrate the effectiveness of different technology suitable for use with high salinity flow back brines and produced water. The design of the mobile unit is based on previous and current work at the Texas A&M Separation Sciences Pilot Plant.

The goals were in two categories for the field trial. First the reduction or removal of specific ions, compounds or materials from the produced water and second the optimization of treatment for reduction in media/membrane replacement and operations cost.

The A&M program was designed first to identify and second to demonstrate that membrane technology could be used to "condition" the brine characteristics of the Marcellus Shale brine at the outflow of the final stage of the process. (The target goals shown in the Table 1 (page 6) are comparative values to the results found in the Texas A&M New York Field trial in 2011). An additional aim was to obtain the approximate cost of such treatment.

Technologies Utilized in Trials

The several treatment techniques which have been found to be successful in both pilot plant and field tests have been tested to incorporate into a single multifunctional process train. Eight different components were evaluated during the trials, two types of oil and grease removal, one BTEX removal step, three micro-filters, and two different nano-filters. The performance of each technique was measured by its separation efficiency, power consumption, and ability to withstand fouling.

Results of the Trial

The field trials were a qualified success. In Pennsylvania, the brine was converted to oil-free, solids-free brine with no biological activity. Microfiltration removed solids effectively including biological in the brines. Nano-filtration in one of the trials successfully reduced the divalent cationic strength approximately 50% in one trial.

Based on a power cost of $.10 per kWh and using averages of three A&M field trials of ultra-high salinity brine, media pretreatment power usage averaged $0.004 per barrel, solids removal $.04 per barrel and brine "softening" $.84 per barrel. Total power cost was approximately $1.00 per barrel of fluid treated.

More details of the project can be found at

https://sites.google.com/site/amgpribgexcogroupfieldtrial/

Recommendations for Treatment of Produced and Frac Flow Back Brines

The Worthington Co. extended duration field trial was the culmination of a three year effort to identify pre-treatment methods for Marcellus Shale brine. Trials in New York (Chenango Co.) and in Pennsylvania (Washington Co. and Worthington Co.) afforded opportunities to evaluate various methods of brine treatment. The technology, commonly referred to as "pre-treatment" is an important component of the trend to re-using frac flowback brine and produced water in oil and gas drilling operations.

Our results show that pre-treatment is achievable and eminently practical. We recommend strongly that well designs for new drilling in the Marcellus take advantage of the copious quantity of brine waters available. Our recommendations come with a specific recommendation; this water to be re-used must be treated to remove certain contaminants if the subsequent well operations are to be the most productive. Our findings showed that the presence of iron, both dissolved and un-dissolved is a problem. Our experience at the Worthington Co. site showed the importance of avoiding or providing a means of reducing the microbial loading of the brine.

These findings lead to some specific recommendations.

1. Incorporate a corrosion inhibitor package in fracturing operations,
2. Monitor corrosion in production wells so as to prevent or minimize damage from corrosion,
3. Use biocide protection in fracturing operations.
4. Monitor produced and frac flow back brines for the presence of biological activity.
5. Defer re-use of produced brine until remedial treatments can be implemented. (Even if the flowback brine is diluted with fresh water as a makeup fluid, the risk of biological contamination in the well is too great to incur.)
6. Consider brine treatment to "soften" the produced water, subsequent brines are more readily incorporated into frac fluid packages.

Appropriate Technology for Application in Marcellus Shale in Worthington Co. PA

Introduction

Shale gas development relies heavily on the hydraulic fracturing process in order to maximize the economic viability of each new well. The challenge is to identify technologies and approaches for treating the frac water that returns to the surface following a frac job (frac flowback water) for beneficial re-use in other applications, thereby conserving other local freshwater supplies. Texas A&M and its partners were funded to identify appropriate technology for brine treatment and to demonstrate the technology in field trials. Treatment consisted of eight (8) tasks to demonstrate frac water pre-treatment technology's ability to remove constituents from the high salinity flowback water and produced brines encountered in the Marcellus region—and accomplish this with minimal chemical usage and no adverse environmental impact.

Aim of the A&M Project

The goal of the A&M Program is to develop a mobile, multifunctional water treatment capability designed specifically for "pre-treatment" of field waste brine by conducting a side-by-side comparison between this new technology and that already existing in field operations. To accomplish this, the A&M team with its partners, tested a number of processes designed to remove contaminants from highly saline brines. Once components of a process train were identified and tested, a mobile testing laboratory was designed and constructed to allow extended duration tests to be conducted in the field.

The trial was to test and demonstrate that the selected technology could be used to "condition" the brine characteristics of the Marcellus Shale brine at the outflow of the final stage of the process. These target goals are comparative values to the results found in the Texas A&M New York Field trial in 2011. A technical paper of that trial is included in the Appendix (page 17).

Table 1 Target Values of Treatment

Characteristic/Item	Reduction or Target Value
Hydrocarbon Reduction	80% reduction
Turbidity	1 NTU or less
Total iron	22% reduction
Hardness Ca^{++}	50% reduction
Barium	44% reduction
Sulfate B/A	77% reduction

A comprehensive analytical test program was planned to provide on-site monitoring of the process. As the program has matured, a new goal has been identified, to seek out and utilize the most appropriate field workable analytic methods for analyzing the performance of the system in operations.

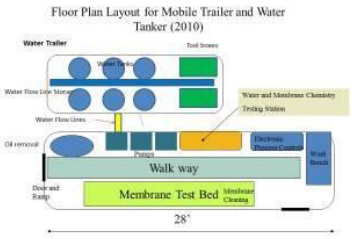
Description of the Mobile Laboratory/Water Treatment Unit

Leading up to the 2012 field trial, A&M's laboratory testing program identified the processes most appropriate for the hyper-saline flow back and produced brines encountered in Marcellus completions. In the first quarter of 2011, the final design was used to construct the process train in the mobile laboratory. Prior to selection of the laboratory's components, pilot tests were conducted to assure the performance standards would be met. Pilot tests prior to Worthington Co. also gave the A&M team experience in monitoring performance of the component and in selecting the most appropriate analytic test to employ in field operations.

The Process Train

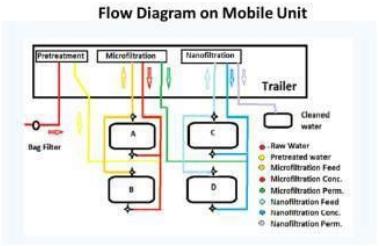
Figure 1 shows the components for the mobile unit. The floor plan layout shows how all tanks and fluid storage are located outside the laboratory but within the environmental pad (18" berm around the pad). The next graphic shows the process train components, each set in the system as a module so as to allow a "plug and play" option for different technologies. The third graphic shows the flow system for the process train. Each step of the process requires different pumping requirements. Media removal of hydrocarbon requires low pressure, low volume pumping rates. Solids removal with microfiltration requires low pressure high rate pumping. Dissolved solids removal (either nanofiltration or reverse osmosis) requires high pressure high rate pumping. The final graphic shows the analytical scheme used to monitor performance of the system.

Figure 1 The Mobile Unit's Design Features

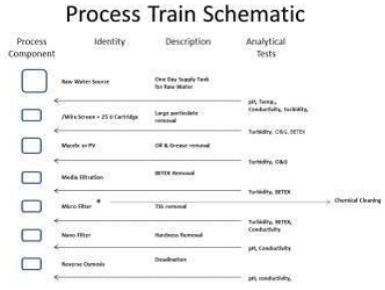


Layout of components in mobile unit.

Components of the process train.



Flow Diagram of the process train - recirculation



Analytical scheme for the components.

The process system was designed to provide an outlet flow capacity of 2 gpm under normal operating conditions. Because membranes require high crossflow velocity, separate flow loops were required. The set of schematics below in Figure 2 shows the layout of the inside of the trailer.

Figure 2 Mobile Unit Interior	
The interior of the membrane trailer shows media filres (in background), low pressure membranse (middle ground) and high pressure spiral wound filters (foreground). On-line monitoring sensors are also shown.	

Analytical

A comprehensive analytical test program was established in cooperation with Texas A&M TEEX Water and Wastewater Training group. Keith McLeroy (instructor at the MI SWACO Analytical Training Workshop) formerly worked 25% of the time for the Desalination Project. By utilizing on site, real time monitoring of process train performance we increase the efficiency of the brine treatment and increase lifetimes of the components.

Media Filtration/Hydrocarbon Removal (Figure 1)

The mobile unit incorporated a data-acquisition system that monitors flow behavior, pressures, water quality and power loads (kWh or hp) of the various pumping and treatment combinations of water pretreatment. The media and the micro-filtration systems were designed to operate below 100 psi, thus reducing construction costs and lowering power costs of the low pressure pumping system. Nano-filtration pumping was designed for 1,000 psi. The "thoughput-gpm" depends upon the separation efficiency of the component which depends upon the composition of the raw water stream. The higher the salinity, the more energy is needed to pump brine through the membranes

Mycelx Inc.[1] provided filtration to remove oil and grease. The filters performed successfully in pilot plant tests and were installed in the mobile laboratory. Polymer Ventures Inc.[2] has also provided filtration to remove oil and grease. Multiple trials in pilot plant tests have been encouraging and so the filters are included as one component in the mobile lab.

[1] http://www.mycelx.com
[2] http://www.polymerventures.com

ABS Systems Inc.[3] has provided a commercial product to remove BETX. A&M also tested an alternative to the ABS material in an earlier trial in Washington Co. using a synthetically modified zeolite material obtained from the Los Alamos National Laboratory[4], a modified naturally occurring material designed to remove oil and grease from waste streams. We found the material to be effective and removed over 90% of the BETX in the pilot plant trials of the process system. It was included in the mobile lab process train.

Membrane Selection Tests

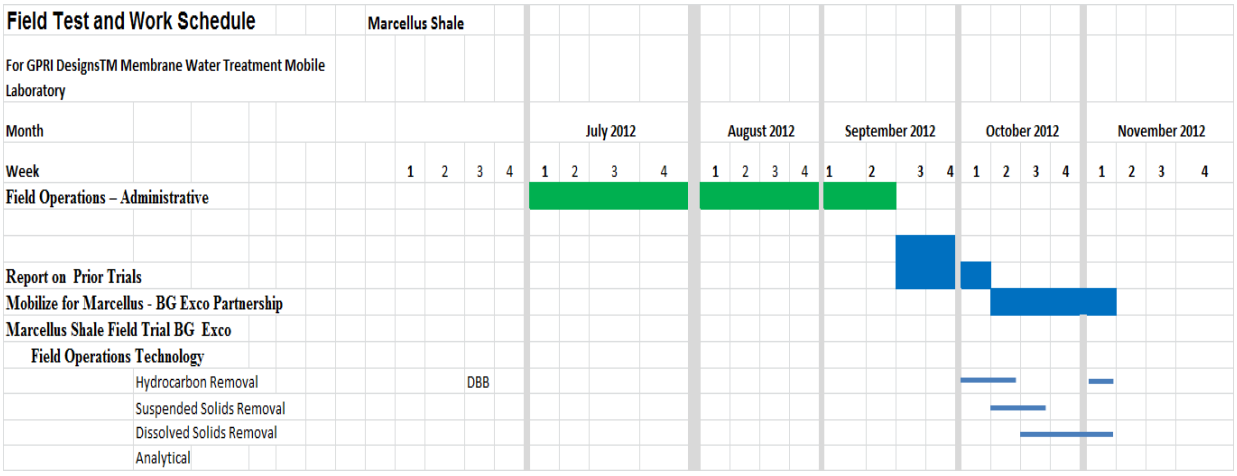
Koch ceramics were used in the mobile lab**.** This filter along with Pall hollow fiber membranes and stainless steel membranes were all tested in both the A&M pilot plant and previous field trials (Appendix 2) The key to success of the filters are their ability to be cleaned by back flushing and washing with chemical cleansing agents.

Dow Chemical nano-filters were one of the membranes chosen for mobile lab and were tested successfully in numerous pilot plant tests. Feed brine for these membrane filters must be free of dissolved solids as they are configured in a spiral wound configuration and are not amenable to back flushing or chemical cleansing. The trial also tested membranes from GE and from Hydranautics

The Schedule of the Program

Table 2 shows the Task Schedule for each step of the project in Worthington Co. (A delay at the outset of the trial was an administrative stay.) Field staffing for the tasks was GPRI personnel, all trained in safety and OSHA field ops. All work performed was under the supervision of senior A&M staff.

Table 2 Test Schedule



Description of the Field Trial

Analyses Brine

The brine analysis of the Claypool site was provided by Exco Resources, the operator of the site. Table 3 shows that recent compositional analysis. Total dissolved solids at less than 70,000

[3] http://www.pwabsorbents.com/ (transitional web link)

[4] http://www.netl.doe.gov/technologies/oil-gas/Petroleum/projects/Environmental/Produced_Water/15461.htm

mg/L is not especially high but both the total hardness and the organics in the brine indicated that the brine's quality would be problematic for re-use as a frac fluid without treatment.

Table 3 Brine Analysis

Laboratory Results Geochemical Testing

Date: 22 Aug. 2012
Location: Calypool Frac Flowback Pond - BG Exco Partnership, Worthington Co. PA
Lab: *Geochemical Testing , Somerset PA*

Analyses

Inorganic non-metals	**Results**	**Units**
Acidity	69	mg/L CaCO3
Physical Tests		
conductance	91200	umhos/cm
lab pH	6.69	
Inorganic non-metals		
total dissolved solids	68700	mg/L
total suspended solids	5	mg/L
Indicator Organic Materials		
BOD 5-day	1100	mg/L
chemical oxygen demand	6700	mg/L
Inorganic non-metals		
bromide	394	mg/L
chloride	69,700	mg/L
sulfate	<2	mg/L
Inorganic Metals		
Iron, dissolved	59.7	mg/L
Arsenic	<1	mg/L
Barium	421	mg/L
Calcium	6,270	mg/L
Iron, total	85.8	mg/L
Magnesium	565	mg/L
Sodium	23,900	mg/L
hardness	18,000	mg/L CaCO3
Volatile Organics		
Benzene	102	ug/L
Toluenes	177	ug/L
Organics		
oil & grease	209	mg/L

While not available at the outset of the A&M field trial, it was necessary to get estimates of biological activity in the pond because of the detrimental effect of organic bacteria as plugging or fouling agents. Table 4 shows a bacterial analysis performed during the A&M trial to test the performance of the experimental ultra-filter. Further descriptive information is available in the *Results of Testing* Section. (A copy of the Analysis is contained in the Appendix.) Results show high biological activity which indicates a problem of concern.

Table 4 Microbiology Analysis[i5]

Coliform	Method SM 9223B	See below per 100 ml
E coli	Method SM 9223B	See below per 100 ml
Heterotrophic Plate Count	Method SM 9215B	> 5700E cfu per mL

Procedures

Field ops were performed in the following manner. The first test series (tests 1 and 2) were performed to measure the ability of different materials to selectively remove hydrocarbons and other petroleum components from frac pond brine.

Test 1 was conducted at a flow rate of 2gpm through the media filters. Initial frac pond brine was pumped through a sock filter (10 micron nominal), and then Mycelx media filter then ABS BETX removal. Filtrate (permeate) was collected in an oil free brine tank

[5] [5] Microbac Laboratories Inc. Report 2101705, 10.26.2012 (Appendix 2)

("Tank 1") for subsequent micro filtration.

Test 2 repeated the first test except that a Polymer Ventures filter was substituted for the Mycelx filter.

The second test series (tests 3, 4, and 5) evaluated the effectiveness of the micro-filters to remove solids (TSS).

Test 3 evaluated TSS removal of a ceramic filter. This filter utilizes cross flow filtration at high pump rates to reject solids greater than 0.2 micron in size. Oil-free brine was pumped from Tank 1 across the filter and permeate collected in a solids free poly tank ("Tank 2") on the water trailer adjacent to the mobile laboratory. Samples were taken for turbidity measurement.

Test 4 was conducted in the same manner as test 3 with the substitution of the Grave stainless steel micro-filter.

Test 5 was conducted in the same manner as tests 3 and 4 using a hollow fiber micro-filter for solids rejection.

The last test series measured the ability of the nano-filter to remove certain dissolved solids (salts) from the solids-free brine.

Field Trial Results and Data

Results of the test sequences are shown in Table 1. The test sequences refer to the arrangements of the process train. The design of the system requires three sequential operations (1) oil removal (hydrocarbon) removal, (2) suspended solids removal, and (3) dissolved solids reduction (softening).

Guard filter Pre-treatment

Raw brine from the frac flow back pond was pumped first through a screen filter and a 10 micron (nominal) cartridge filter to remove large particulate material step (1). This "guard" filter is used as a precaution step to minimize any depth solids plugging of the media filters just downstream. The brine was then pumped directly through the media filters at a flow rate of 2 gpm (step 2).

Oil and BETEX Removal

Media filters were sized (bulk volume) to allow specified residence time to maximize oil removal. Three media materials were evaluated. Samples were taken for analysis of oil content. Two materials are known to remove oil and grease, filters from Polymer Ventures, and cartridges from Mycelx Inc. and material (ABS Services) were evaluated in separate steps. Table 5 shows results. After sufficient oil free brine was collected, a separate pumping system directed the brine through the next step, microfiltration.

Table 5 Media Removal of Hydrocarbons

PreTreatment		Pre-treatment consists of 10 micron screen then oil and grease removal step followed by BTEX removal						
Sample No.	**Sample Identification**	**Turbidity, ntu**	**Total Iron**	**TDS, ppm**		**pH**	**TOC**	**Comments**
SP-1	media pre-treat	307	60	68,700		6.7	92	Raw water
SP-2			---	---		---	61	Output brine
SP-3		357	60	68,700		6.7	98	Raw water
SP-4		264	---	---		---	63	Output brine
		254 (after ABS)						

The data show by comparison of before and after values of TOC that the hydrocarbon removal was noticeable—approximately 30% reduction in value. Subsequent laboratory analyses of bacterial loading (high) would infer that the majority of the organic carbon was in the form of biological substrates. Reduction in values of turbidity was also noticeable. Since these media are not designed to be depth filters to remove suspended solids, this is acceptable and actually preferable since plugging would result if the media were blocked by fouling suspended solids.

Suspended Solids Removal

In water treatment, the primary cause of field failure is inadequate design of solids removal. The key to successful adoption of micro-filtration for solids removal lies in the design of the process train that avoids filter fouling. One feature of the A&M system is the use of micro-filtration to remove suspended solids from the brine stream. The A&M work is based on Canadian research and early commercial systems by Osmonics for municipal water treatment.[6]

Texas A&M began a program in the early 2000s to develop commercial process trains. By eliminating the conventional flocculation, precipitation, and filtration step, the process train provided a more compact system and one that uses fewer chemicals. The system being trialed in the Marcellus Shale has been tested for over 5 years in the pilot plant and in earlier trials.

Micro porous membranes are designed to retain all particles above their pore size ratings, while a asymmetric membrane is characterized by a thin skin on the surface of the membrane, rejection occurs only at the surface, and retained particles above the nominal molecular weight cut-off (MWCO) do not enter the main body of the membrane MWCO is the ability of a membrane to reject the species of certain molecular weight measured as Daltons.

Spiral wound and hollow fiber MF membranes are made of polymeric materials, for the most part asymmetric and a list of commonly used polymers includes Teflon (PTFE), polyvinylidene fluoride (PVDF), cellulose acetate, polysulfone, nylon and polycarbonate. Non-polymeric submicron membranes manufactured from durable materials such as ceramics and metallic are also used for MF separation. UF membranes provide a more complete rejection of materials, including some high molecular materials such as soluble, high molecular weight synthetic materials UF membranes are typically asymmetrical polymeric membranes like the MF membranes.

The A&M system uses UFs that can be reverse washed to reduce fouling. Best results were found with pressurized hollow fiber, ceramic, and a stainless steel. The field trials offer a way to

[6] http://connection.ebscohost.com/tag/OSMONICS%2BInc

differentiate the effectiveness of the alternatives therefore all three types were employed in the trial, ceramic, stainless steel, and capillary hollow fiber.

The system monitors filtration rate as a function of throughput (elapsed time). The data acquisition recorded turbidity (NTU) upstream and downstream of the filters. Finally the output flow rate was recorded at periodic intervals.

Commercial Systems Offering Micro-Filtration Systems for TSS Removal

While A&M pioneered use of microfiltration for TSS removal, the practice is becoming more popular as commercial water treatment companies have embraced the concept. Siemens is offering high level systems designs for waste water treatment.[7]

In addition, GE (who purchased Osmonics in the early 2000s) now offers commercial services through its Water and Power Division.[8]

Finally Koch Industries has just offered commercial hollow fiber micro-filter units that have reportedly performed well in field applications. A&M will be testing these filters for the EFD-TIP program in 2013.

Following are charts and a summary of TSS removal and filter efficiency. Turbidity readings before and after filtration show very good solids removal (any NTU value of less than 3 is considered acceptable for subsequent spiral wrapped membrane feed). The spreadsheet enclosed contains incremental data --charted in the following plots.

In this process train, cross flow micro-filtration as used to remove solids to the sub-micron level, a necessary step prior to membrane treatment. In previous field trials, three types of micro-filters were tested in the process train, (a) ceramic, (b) stainless steel, and (3) hollow fiber filters. (These filters can be backwashed and cleaned easily, making them the best candidates for TSS removal.) However for the Worthington Co. test, our process train was equipped with hollow fiber micro-filters from Koch Industries. This selection was made because of the superior TSS rejection and relatively high flux rate afforded by this configuration.

Table 6 shows the analytical results of the comparison tests of before and after micro filter tests. The "before" samples (odd numbered samples) had oil and grease and BETX removed by media filtration. Since this step in the process train has been designed to remove suspended, the value for turbidity (NTU) is the important piece of data in the Table. For instance the first sample (sm 1) had a NTU value of 277 while the outlet sample (sm 2) had a NTU value of 0.5. A second significant observation that can be made from the data is the consistency of the performance of the micro-filter over an extend time period. .

[7] http://www.water.siemens.com/en/products/membrane_filtration_separation/Pages/default.aspx?stc=wwiis250082

[8] www.gewater.com/pdf/1143927-%20Lit-%20Sepa%20CF%20II.pdf

Table 6 Micro-Filter Data

Koch microfilter										
Sample No.	Sample Identification	Turbidity, ntu	Total Iron	TDS, ppm	Conductivity, ms/cm	pH	TOC	Comments		
SM-1	Pre-treated feed	277	55	68,000				Before filter		
SM-2	MF permeate	0.5	31	65,300		6.71		After filter		
SM-3	Pre-treated feed		33	43,200	5.76	6.79	126	before and after samples sent to lab for bacterial analysis		
SM-4	MF permeate		24	42,500	4.25	7.27	48.8			
SM-5		339	31.7	44,400	4.44	6.42	62.9			
SM-6		1.1	20.2	42,500	4.25	6.7	39.6			
SM-7	Concentrate feed	378	33	42,800	4.28	6.8	52.5	pre-treat tank		
SM-8	MF permeate	0.6	21	43,300	4.37	6.9	42.5			
SM-9	Concentrate feed		30.3	41,300	4.46	7.1	98.1	concentrate		
SM-10	MF permeate		22.5	42,700	4.13	6.4	64.9	next day tested		acidized
SM-11	Concentrate feed		26.4	43,700	4.37	7.05	101	Before filter		
SM-12	MF permeate		24	43,100	4.31	6.8	55	After filter		

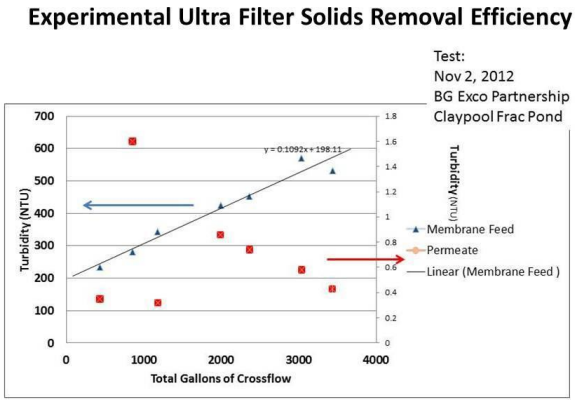
Experimental Ultra-Filter Solids Rejection

In 1992 Zaidi, Simms and Kok reported tests of ultra-filters for removal of oil and suspended solids but few commercial systems have been developed[9]. The field trial provided GPRI the opportunity to test a new type of ultra-filter provided by a membrane manufacturer specifically for the treatment of produced water. The filter, a spiral wound standard sized membrane, is designed to be used with untreated brine and has the capability of removing all suspended solids (TSS) as well as a significant amount of hydrocarbon present in the process brine.

In two days of testing with untreated frac pond brine showed the filter showed little evidence of fouling. The untreated brine turbidity values ranged from approximately 100 to greater than 700. Permeate values were less than 2 in all cases.

[9] Zaidi, K. Simms and S. Kok *The Use of Micro/Ultrafiltration for the Removal of Oil and Suspended Solids from Oilfield Brines, Water Science & Technology* Vol. 25 No 10 pp. 163–176 © IWA Publishing 1992

Figure 3 Experimental Ultra Filter Solids Removal Efficiency



The blue triangles represent the turbidity of the inlet feed brine while the red squares show the permeate turbidity (the right vertical axis). Significantly more testing is planned at the A&M Riverside Pilot Plant.

Environmental laboratory results showed that bacteria counts were lowered by more than 5 orders of magnitude by the filter. (Appendix 2). Table 7 shows before and after bacterial counts

Table 7 Microbiology Analysisii[10]

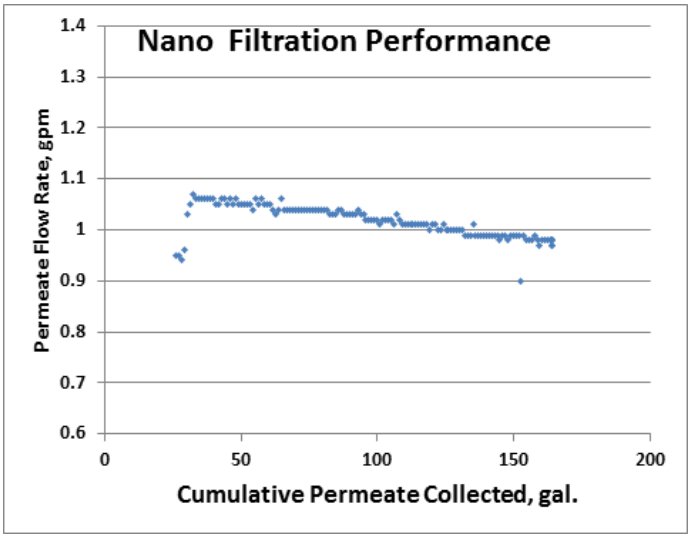
Before Ultra Filtration		Relative Decrease
Heterotrophic Plate Count	> 5700E cfu per mL	
After Ultra Filtration		
Heterotrophic Plate Count	1E cfu per mL	5 orders of magnitude

Membrane Treatment to Remove Dissolved Solids

Nanofiltration (NF) is used in high salinity brines to reduce salinity and selectively remove certain divalent substances, such as sulfates and heavy metals. Flow testing measures the ability of the membrane to perform for extended periods. The chart in Figure 4 shows the flux rate of Hydranautics filter during one morning's run. The observed flow reduction was approximately 5%. Such reduction is typical and can be recovered by flushing with clean brine.

[10] [10] Microbac Laboratories Inc. Report 2101705, 10.26.2012 (Appendix 2)

Figure 4 Nano Filter Performances.



The nano-filtration step is designed to reduce the ionic content of key divalent ions such as iron and sulfate. Permeate solutions are designed to be stable because of the lower ionic strength. In the case of the Worthington Co. tests, the nano-filtration was not effective. However in previous field trials, our results were more favorable as shown in Table 8. A comparison of before and after dissolved ion removal in an early trial in New York shows effective softening. Those field results were not repeated in Pennsylvania. A review of test procedures indicated that the nano-filter was operated at a pressure below nominal and thus was less efficient. Further testing in 2013 is planned.

Table 8 Dissolved Ion Removal by Nano Filtration

		Raw Feed	Permeate	Comments
Samples	**Analyte**			
SN7, SN8	Sulfate	1025	92	Trial 1 Dow N-245 (A)
"	Chlorides	186,500	150,000	Trial 1 Dow N-245 (A)
"	Hardness	67,200	51,600	Trial 1 Dow N-245 (A)
SN60, SN 6	Iron (Fe)	183	103	Trial 1 Dow N-245 (A)
S-60, S-61	Barium - B	183	103	Trial 1 Dow N-245 (A)
SN1, SN2	Iron (Fe)	20.5	18.5	Trial 3 - Hydranautics NF
SN3, SN4	"	21.4	18.6	"
SN5, SN6	"	22	19.1	"
SN7, SN8	"	20.2	17.8	"

Conclusions and Recommendations

Overall, the field trial was a success. The process train tested by GPRI operated successfully for over a month with few problems. The media filters performed adequately and lowered hydrocarbon content to such a value as to cause no fouling problems with downstream filters. The microfiltration membranes all functioned satisfactorily to remove suspended solids with turbidities ranging up to 500. The experimental ultra-filter performed above expectations and is being included in 2013 trials. However brine softening with the nano-filter used to reduce

alkalinity was below par. The problem stemmed from an operational error that allowed the filter to operate at below optimal pressure. Because the nano-filter has performed satisfactorily in previous pilot plant and field trials, it is assumed that the Worthington test was an anomaly.

The cost of pre-treatment can be estimated by observing the energy required to pump brine through the system. Based on a power cost of $.10 per kWh and using averages of three A&M field trials of ultra-high salinity brine, media pretreatment power usage averaged $0.004 per barrel, solids removal $.04 per barrel and brine "softening" $.84 per barrel. Total power cost was approximately $1.00 per barrel of fluid treated.

Table 9 Cost of Powering Process

Samples	Date	Test Description	Duration	kw used	cost per bbl
S-62, S-63	Sept. 2	Running Dow NF (B)	3.35	0.2	$ 0.84
S-58, S-59	2-Sep	Koch U-F			$0.0275
S-84, S-85	Sept. 20	media	325 gal.	0.3	$ 0.0039
		Koch UF	63.63	2.1	$ 0.14
					$ 0.98

Acknowledgements

Texas A&M has several partners who both sponsored and provided equipment and services to the development of the mobile unit. These partners assisted in the trial and contributed to its success, notably MI SWACO Schlumberger, Texas A&M EEI (Energy Engineering Institute), TEES (Texas Engineering Experiment Station), TEEX (Texas A&M Engineering Extension Service), and the EFD (Environmentally Friendly Drilling) program at the Houston Advanced Research Center (HARC). Dow Filmtec, Hydranautics, Koch Filters, Graver, and Pall (all filters) and ABS Systems Mycelx, and Polymer Ventures (media filtration) all provided products for testing. The project allowed for the identification and utilization of new and advanced analytic techniques suitable for field application. Three companies field services, GIS Environmental, INFICON, and Hach Chemicals who provided analytical services. Duke University assisted with sampling and performed analysis of radio-nucleotides. Colgate University helped with providing local service and support.

Appendices

Claypool Water Analysis

Microbiological Report

SPE 158396PP Burnett, et al

APPENDX 1

" Pilot Testing Pre-Treatment Options to Allow Re-Use of Frac Flowback and Produced Brine for Gas Shale Resource Development"

Final Report

Prepared by

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New York State Energy Research and Development Authority
Prime Awarding Agency
Project No. 17438 PO#ERDA1-0000018675

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FIGURES

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Executive Summary

In this report, we summarize the results of pilot testing to evaluate the effects of pulsed, high frequency electromagnetic fields as a strategy to mitigate fouling and flux decline during the filtration of flowback water. Our approach was to evaluate the effects separately on organic foulants, bacterial solutions, and inorganic scaling solutions, and then in combination in synthetic flowback water solutions. Membrane modification via graft polymerization of vinyl monomers on to poly(ether) sulfone UF membranes was evaluated as a route to mitigate fouling by components in hydraulic fracturing flowback water. A new gallium-based biocide was evaluated as a way to control biofilm formation and biofouling on membrane surfaces. Finally, a model to predict the transport of small organic molecules in nanofiltration membranes was developed to predict the effectiveness of such membranes in removal of residual organics in a flowback treatment train.

The effects of the Dolphin system were evaluated using a number of filtration tests. Organic, biological, and synthetic flowback foulants were tested at various concentrations, pH and ionic strength values. The Dolphin module had the largest effect on solutions near optimal aggregation conditions. This was observed for Aldrich Humic Acid and a synthetic scaling solution. The oscillating electromagnetic field reduced the effects of fouling by slowing down permeate flux reduction and inducing particle aggregation. For the scaling solution this was verified by differential light scattering. The Dolphin system had little effect on fouling by low-molecular weight Suwanee River natural organic matter, sodium alginate, a model polysaccharide, or dextran as model organics. The Dolphin system worsened fouling by *Pseudomonas putida* bacterial suspension. When the Dolphin system was activated there was a larger flux decline; possible explanations include acting as a stressor that induced production of extracellular material (polysaccharides or proteins) that exacerbated fouling, or partial lysing that resulting in exposing the membrane to internal cell components (proteins, etc) that acted as foulants. In addition, the Dolphin system has little impact on flux decline exhibited by an oil emulsion and a synthetic flowback solution.

Flux decline data was modeled using kinetic models that account for pore blockage and cake filtration. Plots of total resistance as a function of time were generated for each filtration experiment and the values of the kinetic constants for each fouling mechanism were evaluated. For most data sets, the cake formation rate constants were greater under higher ionic strength conditions, and when the Dolphin system was not activated. The lower cake formation rate constants found when the Dolphin was activated are likely due to the aggregation effects induced by the electromagnetic field. However, the pore blockage parameters were similar. These trends were observed for all organic solutions and for the scaling solution, but not for the oil emulsion or synthetic flowback solution.

We used atmospheric pressure (AP) plasma-induced graft polymerization to modify polyethersulfone (PES) membranes, employing a high throughput approach to discover suitable surface chemistries that could reduce the effects of fouling by sodium alginate and synthetic flowback water solutions. Monomers for the graft polymerization reactions were extracted from a library of 66 vinyl monomers. These monomers belonged to three categories: amines, polyethylene glycols (PEG's), and basic & zwitterionic. Fouling effects were quantified by a fouling index, defined as the ratio of the resistance difference between the fouled and unfouled membranes for the modified and control (unmodified) membranes. Low fouling indices were found using a zwitterion, 2-(methacryloyloxy)ethyl trimethylammonium sulfate, for both sodium alginate solutions and model flow back water. These findings suggest promising alternative solutions to dynamic fouling focusing primarily on surface chemistry.

We have evaluated gallium chloride, $GaCl_3$, as a biocide to control biofilm formation and hence fouling on membrane surfaces. We employed a metal-reducing bacterium, *Shewanella oneidensis* MR-1, because it is known to produce a strong biofilm that enables electron transfer from the medium to its outer membrane. We compared biofilms grown using either Fe(III) nitrilotriacetic acid (Fe NTA) or $GaCl_3$ as dissolved electron acceptors. Biofilms were grown on glass slides in a biofilm drip reactor using lactic acid as a primary electron donor (carbon source) in the system. Biofilms grown on Fe NTA showed a dense biofilm with significant production of extra polysaccharides and a seemingly stable bacterial population, whereas the biofilms grown on $GaCl_3$ were weak and dispersed, lacking extrapolymeric substances. These results indicate that gallium chloride is an inhibitor of biofilm growth, and seems to be a promising and novel biocide for biofilm control.

We developed a transport model to quantify rejection of organic constituents present in flowback water by nanofiltration membranes, incorporating the effects of adsorption, a novel feature of this work. This study provides valuable insights into future experiments on the removal of chemical additives. We found that pH can significantly impact the adsorption of ionizable organics, as expected. Rejection was observed to depend on both molecular size and charge (electrostatic repulsion). The dynamic model developed can predict the breakthrough behavior of phenol on three membranes, with a slight overestimation of rejection and underestimation of the retention time, which may be explained by the affinity of the molecules to membrane. 2,4-dinitrophenol (DNP) showed a much smaller adsorption tendency in filtration experiments than in batch sorption experiments. A possible explanation is the effect of charge in a confined pore. The rejection of both phenol and 2,4-DNP were overestimated by the model, which could be explained by the underestimation of partition coefficient, which correlated with the adsorption affinity. Flux decline was modest (with the largest value around 7%), and was consistent with the adsorption experiments.

1.1 Introduction

Shale gas has become a more important natural gas source in the US, and is poised to become even more so. Unlike the conventional production of natural gas, shale gas is more difficult to remove from the ground. Shale formations contain very tight rock, with less pore space than traditional oil and gas formations [Veil, 2010]. To address this problem, horizontal drilling and hydraulic fracturing techniques have been developed. Horizontal drilling is critical for producing shale gas because it creates a well that penetrates a large portion of the shale formation, allowing for the efficient collection of gas [Veil, 2010]. A Marcellus well in New York State would likely be drilled vertically to a depth of 4,000 to 6,000 feet, and extend horizontally a comparable distance through the target shale formation [Wright et al., 2010]. Hydraulic fracturing is the process to create fractures in the rock formations, increasing the rate and amount of natural gas recovery.

The hydraulic fracturing process involves the injection of water, sand and other chemicals into the well under high pressure. After the hydraulic fracturing is complete, the fluids returning to the surface within the first seven to fourteen days (often called flow back) will require treatment for beneficial reuse, recycling or disposal [Advanced Resources International, 2010]. Flow back fluids include the fracturing fluids pumped into the well, mainly consisting of water and additives; any new compounds that may have formed from reactions between chemical components; and substances mobilized from within the shale formation due to the fracturing operation [UGS Corporation, 2009]. Typically, classes of components of flow back fluid include salts, minerals, metals, bacteria, friction reducers, and acid gases [UGS Corporation, 2009]. Some minerals and metals may be in suspended solid form, as iron solids, dispersed clay fines, colloids and silts. Organics may be dissolved, colloidal, or present as a separate oil phase.

The Pennsylvania Department of Environmental Protection, Bureau of Oil and Gas Management, has compiled a list of potential additives used by hydraulic fracturing companies in Pennsylvania, compiled from Material Safety Data Sheets obtained from industry. Selected chemicals from this list are tabulated in Appendix 1, with their structures and possible uses.

1.1 Treatability and Treatment Techniques

Properties of flowback water are expected to vary by geologic basin, specific rock strata [Wright et al., 2010] and by the additives used to create the injected aqueous solution. However, it is useful to consider available data concerning the components of flowback water [NYSDEC, 2009], from which some general characteristics can be ascertained:

1. Gelling agents, surfactants and chlorides are identified as of greatest environmental concern [NYSDEC, 1992];
2. High total dissolved solids (TDS) (1,530 to 337,000 mg/L, median 93,200 mg/L);
3. Oil and grease in varying quantities (5 to 1470 mg/L, median 17 mg/L);
4. High total organic carbon (TOC) (69.2 to 1,080 mg/L, median 449 mg/L);
5. High Total Suspended Solids (TSS) (30.6 to 1,910 mg, median 146 mg/L);
6. pH < neutral, with a median of 6.2, but ranging from 1 to 8.

To minimize the disposal or discharge of flowback water, the reuse of flowback water should be maximized; e.g., for subsequent fracturing operations at the same well pad or other well pads [NYSDEC, 2009]. This involves dilution of the flowback water with fresh water or more sophisticated treatment options. Three basic issues should be considered [UGS Corporation, 2009]: 1) flowback water composition; 2) specifications for injection water composition; and, 3) disposal of residuals. Several on-site flowback water treatment technologies have been summarized [UGS Corporation, 2009], as tabulated in Table 1-1. In addition to the technologies in Table 1-1, other technologies such as activated sludge aerobic biological treatment [Tellez et al., 2002], wetland treatment [Murray-Gulde et al., 2003] and compacted bentonite membrane treatment [Ranck et al., 2005] have been discussed for the removal of specific components.

Table. 1-1. Comparison of On-site Flowback Water Treatment Technologies.

Characteristics	Filtration	Ion exchange	Reverse Osmosis	Electrodialysis	Thermal Distillation
Energy cost	Low	Low	Moderate	High	High
Energy vs TDS	Independent	Low	Increase	High Incresae	Independent
Plant/Unit size	Small/Modular	Small/Modular	Modular	Modular	Large
Biofouling	Possible	Possible	Possible	Low	NA
Complexity	Low	Moderate	Moderate	Moderate	High
Scaling potential	Low	Low	High	Low	Low
Feed TDS Limit	NA	NA	32,000	40,000	100,000
Pretreatment	NA	Filtration	Filtration	Filtration	Minimal
Product TDS	As feed	200-500	200-500	200-1000	<10
Recovery rate	95%	90%	30 to 50%	60-80%	75-85%

Note: TDS given in mg/L. Based on data from UGS Corporation, Water-Related Issues Associated With Gas Production In The Marcellus Shale: Additives Use, Flowback Quality and Quantities, Regulations, On-site Treatment, Green Technologies, Alternate Water Sources, Water Well-Testing. 2009: Fort Washington, PA.

Membrane processes, mainly reverse osmosis (RO), have been discussed as an option to treat flowback water [Veil, 2010; Wright et al., 2010; NYSDEC, 2009]. A good deal of research has addressed some of the potential components of flowback water: for dissolved solids, NF and RO treatments have been studied for long [Van Hoof et al., 1999];

For oil and grease, pretreatment techniques like coagulation, filtration, MF can be used [Harussi et al., 2001]; for organic compounds, UF and NF can be effective [Karakulski and Morawski, 2002]; for suspended solids, UF is appropriate [Zaidi et al., 1992]. Membranes may be used as-received, or after surface modification to reduce fouling, including biofouling [Zhou et al., 2005].

Electromagnetic treatment has been used in in the cooling water industry to prevent scaling for some time [Cho et al. 1997]. It is thought that the electromagnetic field (EMF) influences the process of nucleation and crystal growth [Alley and Kienle, 2008]. Since no chemicals are needed, this method has some advantages over the traditional chemical treatment. Pulsed, high frequency electromagnetic fields are thought to "activate" suspended particles, including bacteria, by removing the adsorbed charge on its surface. With the adsorbed surface charge removed, suspended particles become favorable sites for adsorption or precipitation. Ions or colloids can then precipitate on the surface or aggregate, forming a powder-like structure, potentially lowering its ability to cause membrane fouling [Clearwater Inc.].

In this research, the effects of an EMF system (Clearwater, Inc.) on membrane fouling will be investigated. Clearwater's technology has a proven track record of eliminating the sources of fouling in cooling water systems. There is some evidence that the Dolphin system is able to prevent fouling from calcium carbonate scale and biofouling [Opheim, 2000; Lane, 2001]. Xiao-kai et al. (2006) demonstrated that nucleation sites are larger and precipitation occurs at a faster rate when the flow loop from a hard water tank is exposed to an electromagnetic anti-fouling module. Conversely, a study conducted by Vidic et al. (2009) showed no positive effect on employing magnetic and pulsed water treatment for the prevention of biofouling in cooling towers. Effects are more clearly seen in studies where the field strength can be manipulated. Kim et al. (2007) found an optimal electric field value for the reduction of membrane fouling and particle coagulation enhancement.

In this final report, we summarize 1) the pilot testing to evaluate the proprietary Dolphin system to reduce flux effects of organic foulants, bacterial solutions, and synthetic flowback water solutions; 2) aggregation assessment by dynamic light scattering (DLS) measurements; 3) work done toward evaluating membrane modification as a route to mitigate fouling by components in hydraulic fracturing flowback water; and 4) work to develop models to predict the transport of small organics in nanofiltration systems.

2.0 Bench Scale Testing: Effects of Pulsed Electromagnetic Fields

2.1 System Design

The cross-flow membrane filtration system is shown in Figure 2-1. The stainless steel test cell has a channel length of 5.56 $\times 10^{-2}$ m, a channel width of 3.81×10^{-2}m, and a channel height of 9.92×10^{-4} m. These channel dimensions provide an effective membrane area of 2.12×10^{-3} m^2 and a channel cross-sectional flow area of 3.78×10^{-5} m^2. Feed solution is contained in a 20 L stainless steel reservoir (Pope Scientific, Saukville, WI) pressurized with nitrogen gas. The flow path consists of a recycle loop with a high capacity diaphragm pump (F-20 Hydra-cell, Wanner) to provide crossflow independent of feed rate, a digital flow meter (Cole-Parmer) to monitor crossflow flow rate, and a needle valve in the retentate line to adjust recovery. A 2.7 μm stainless steel filter (Pall) is located upstream of the needle valve to prevent clogging.

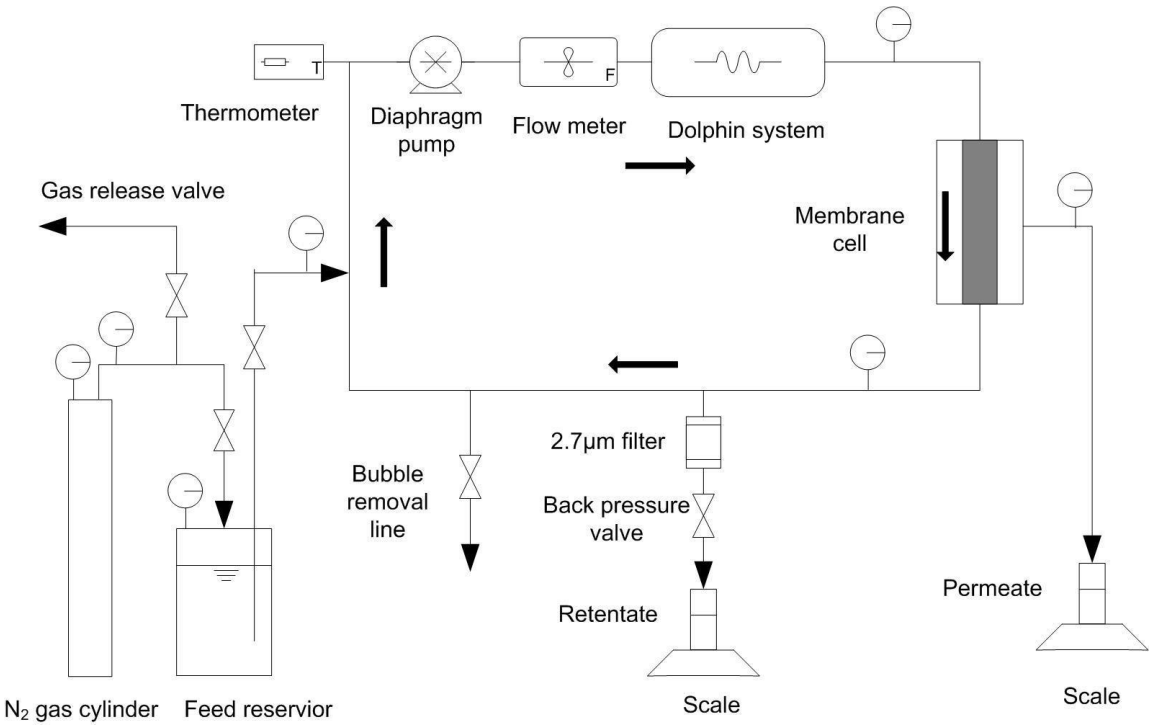


Figure 2-1. Schematic diagram of the cross-flow membrane filtration system.

A literature search was performed to determine typical operating conditions for membrane systems. Selected results are shown in Table 2-1. The cross flow velocity range for such experiment ranges from 0.1 to 0.5 m/s, corresponding to Reynolds numbers from 100 to 500. The diaphragm pump used in our system has sufficient capacity to create a large range of Reynolds number, which will help identify the effects of flow characteristics on membrane process effectiveness.

Table 2-1. Comparison of Experimental Configurations

Ref	Type	Feed	Flow mL/min	Pump	Reynolds Number
Yuan & Kilduff, 2010	NF	Silica colloid/ NOM	227	G	
Yuan & Kilduff, 2009	UF	NOM	681	G	
Ng & Elimelech, 2004	RO/NF	Silica	6,831	D	300-1000
Viadero and Noblet, 2004	MF	fine solids <20–25 micron	10,000	D	0.8
Tarabara et al., 2002	MF/UF	Polystyrene particles 20-680 nm	0-3,000	C	0.116
Comerton et al., 2009a	NF	NOM/CATION	6,000	D	0.8
Comerton et al., 2009b	NF	NOM/CATION	6,000	D	0.8
Lee & Lee, 2007	NF	NOM		NS	1.0
McCallum et al., 2008	NF	model estrogenic hormone	3,750	D	0.4
Mo et al., 2008	RO	BSA		D	0.0914
Gilron & Hasson, 1987	RO	calcium sulphate		D	0.06-0.15
Vrijenhoek et al., 2001	RO	colloidal silica particles, inert organics	950-2,650	D	363-1018
Louie et al., 2006	RO	motor-oil/surfactant/water emulsion		D	
Steinle-Darling et al., 2007	RO	seven nitrosoalklyamines		D	0.1
Comerton et al., 2008	RO/NF	endocrine disrupting compounds	6,000	D	0.8
Choi et al., 2009	RO/NF	Raw water		D	
Jermann et al., 2008	UF	Kaolinite, polysaccharides, humics		G	
Guo et al., 2000	UF	natural DOC, macromolecules, metals		D	
Dai et al., 1998	UF	marine organic colloids		D	
Mcdonough et al., 1998	UF	Silica/polystyrene lattices		G	78-300
Nguyen et al., 2007	UF	highly colored river water		D	
Cheng and Lin, 2004	UF	dextran T500		D	0-0.05
Faibish and Cohen, 2001	UF	oil-in-water (o/w) emulsion		D	1200-10000

Note: Pump type: G = gear; D = diaphragm, C = centrifugal; NS = not specified

2.2 Pilot Testing to Evaluate the Dolphin System

As water flows through the treatment module, the Dolphin imparts pulsed, high frequency electric fields with a reproducible characteristic waveform. In scale prevention applications, it is thought that the Dolphin system changes the electric charge state of suspended particles, and promotes solution phase aggregation and mineral precipitation

thus inhibiting scale deposition on equipment surfaces. The particle/precipitate aggregates formed in solution are more easily cleaned using hydrodynamic forces (flushing).

Dolphin WaterCare is a part of Clearwater Systems Corporation, which has been providing water treatment solutions using patented technology known as The Dolphin system. This system is installed in some 5,000 facilities throughout the world to treat the waters of cooling towers, HVAC and process chillers, ammonia condensers, process heat exchangers, fluid coolers, and hot water systems.

The Dolphin System consists of two main components, a signal generator, which houses the power and control components in a NEMA 3R and IEC IP24 rated enclosure, and a treatment module, which is connected to the signal generator via an "umbilical" cable. The treatment module consists of 1" diameter schedule 80 PVC pipe surrounded by a coil assembly, internal thermal protection switch with automatic reset, umbilical cable, and locking plug connector. The coil assembly is 5" in diameter, and 14.5" in length. Larger treatment modules, which can accommodate higher flow rates, are available.

As water flows through the treatment module, the Dolphin imparts pulsed, high frequency electric fields with a reproducible characteristic waveform. In scale prevention applications, it is thought that the Dolphin system changes the electric charge state of suspended particles, and promotes solution phase aggregation and mineral precipitation thus inhibiting scale deposition on equipment surfaces. The particle/precipitate aggregates formed in solution are more easily cleaned using hydrodynamic forces (flushing).

The Dolphin system has two methods of controlling microbial populations in cooling systems: encapsulation in a mineral precipitate, and electroporation. The electroporation mechanism involves damages to the membranes of planktonic bacteria by the high frequency, pulsing action of the Dolphin System's electric fields by creating small "pores" in their outer membrane. The condition weakens the bacteria and inhibits their capability to reproduce.

We hypothesized that the effects of a pulsed electromagnetic field will include destabilization of colloidal material present in natural groundwater formations and flowback fluid from hydraulic fracturing operations. Particle destabilization will promote aggregation, and increase the effective particle size. It has been shown in the water treatment literature that particle aggregation can have a beneficial effect in membrane processes, reducing flux decline and making membranes easier to clean. Therefore, we hypothesized that the Dolphin system may have a significant role as a pretreatment unit prior to membrane filtration.

2.2.1 Organic Matter Fouling

We tested the effects of a pulsed electromagnetic field on the fouling by solutions of organic compounds. We assessed the reduction in permeate flux and as a measure of overall membrane fouling. We first focused on dissolved organic matter; these solutions were mixed overnight and subsequently pre-filtered using a 0.45µm filter. Membrane filtration was evaluated using a bench scale cross-flow system with either 10 kDa or 100 kDa molecular weight cutoff ultrafiltration membranes.

Suwannee River natural organic matter, Aldrich humic acid, Sodium alginate, and dextran were selected as model organics. All solutions were filtered through a 10 kDa membrane and prepared at the same ionic strength, pH, and foulant concentration. In addition, Aldrich humic acid was filtered through a 100 kDa membrane. Prior to each filtration test, membranes were compacted and conditioned with a 10 mM NaCl solution for at least four hours at 120 psi. The cross-flow membrane system was rinsed with ultrapure water and flushed with a 5-10 mM NaOH solution for an hour after each run. Permeate mass flow was measured using a platform balance with a precision of 0.001 g for the entire duration of the test. Using a membrane area of 0.0018 m^2, the permeate flux was calculated at each data point and plotted against cumulative volume flowing through the membrane. After compaction, permeate flow was measured at a constant pressure of 50 psi with and without the Dolphin system. The permeability of pure water after each filtration run was also measured. As part of the post-filtration procedure, Milli-Q water was used to flush the system as well as to measure pure water permeability after the membrane had been fouled, to provide a measure of flux recovery after cleaning.

Figure 2-2 shows flux decline curves for Suwannee River NOM. With the Dolphin module operating, the permeate flux reduced to 77% of the initial value. When the system was inactive, the permeate flow dropped to 69% of the starting flow rate. Therefore, the oscillating electromagnetic field produced by the Dolphin seems to affect the way NOM deposits on polymeric membranes. This effect, however, only corresponds to a 10% difference in flux, and does not seem to be enough to modify the way organic contaminants interact with the membrane surface.

Representative flux data for the Aldrich humic acid are plotted in Figures 2-3 and 2-4, and representative permeability data are plotted in Figure 2-5. Figure 2-3 depicts the flux decline as a function of time for the Aldrich HA (12 mg/L) filtered on a 10 kDa membrane at pH 4. The effect of the Dolphin system is small under these conditions. It is known that Aldrich HA may begin to aggregate at this pH value, minimizing the effects of the Dolphin in this regard. In addition, the molecular size of the Aldrich HA, even in the absence of aggregation, is likely to be larger than the 10kDa membrane pore size. In combination, these factors result in relatively slow flux decline.

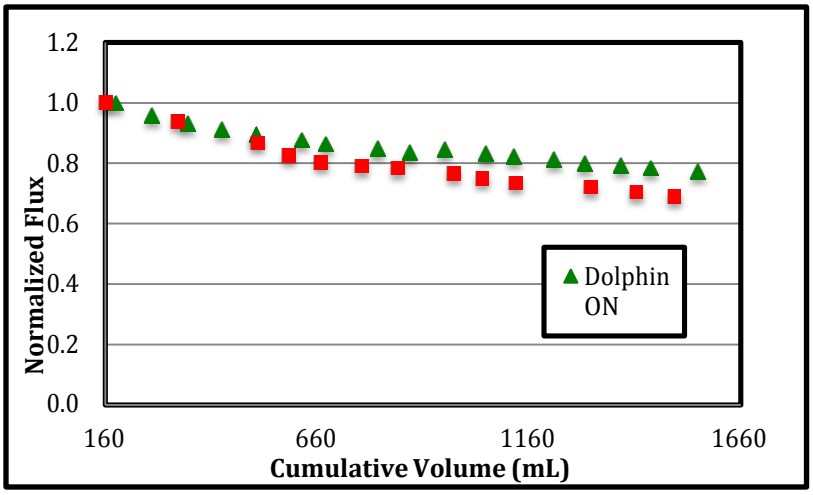


Figure 2-2. Effect of the Dolphin System on the filtration of a 12mg/L Swannee River NOM solution at pH 6.35 in 10mM NaCl.

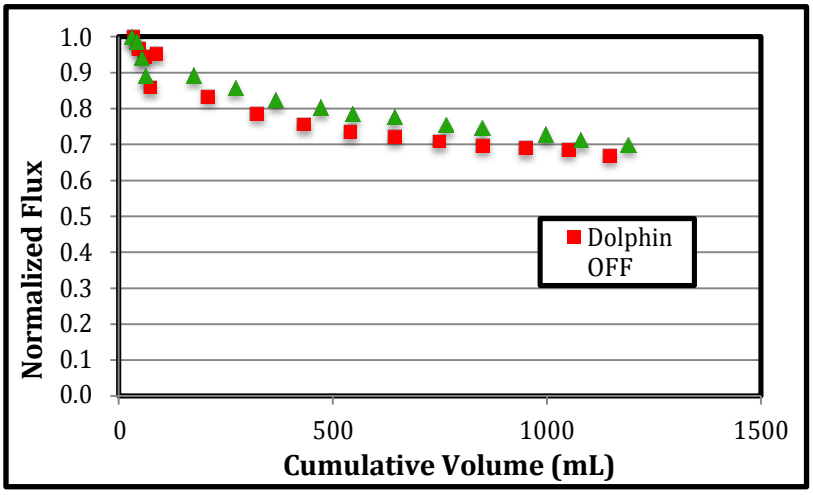


Figure 2-3. Effect of Dolphin System on the Permeate Flux of Aldrich HA using a 10kDa membrane; pH 3.93 at 50 psi.

In contrast, as shown in Figure 2-4, the Dolphin significantly mitigates the flux decline rate during filtration of Aldrich HA by the 100kDa membrane at pH 6. Because the Aldrich HA is expected to be more stable at pH 6, the potential effects of aggregation are more apparent. In addition, it is likely that in a stable (unaggregated) state, some of the HA components penetrate into the 100kDa membrane pores, whereas this may be prevented by the Dolphin system if aggregation is promoted.

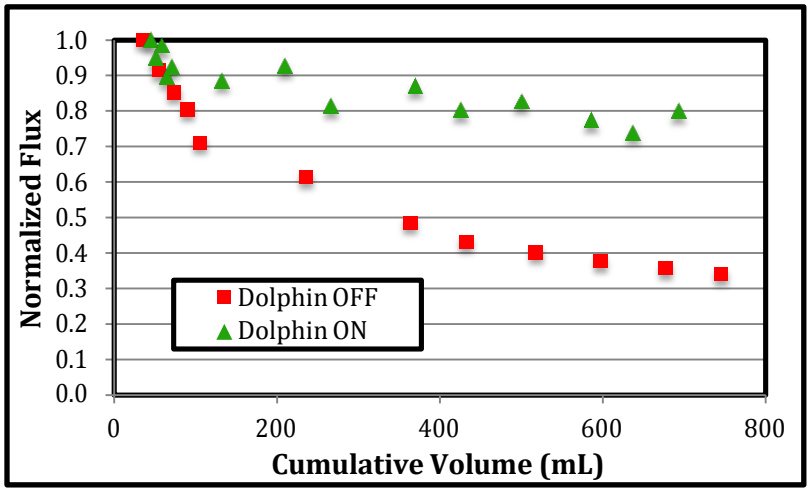


Figure 1-4. Effect of Dolphin System on the Permeate Flux of Aldrich HA using a 100 kDa membrane; pH 6; 51 psi.

Figure 2-5 shows plots of flux versus transmembrane pressure taken after filtration and hydraulic flushing. The slope of this line is the membrane permeability; the higher value shown means that the flux recovery after cleaning was greater when the Dolphin system was operating. These data suggest that the Dolphin System may help reduce the effects of organic fouling on permeate flow and pure water permeability.

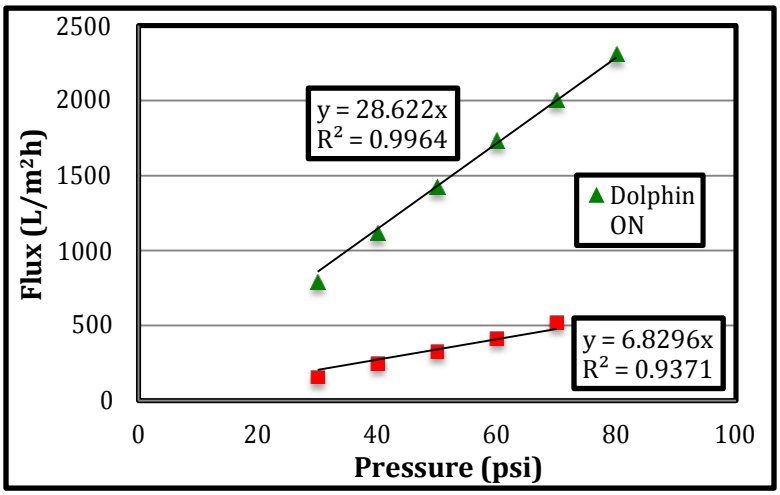


Figure 2-5 Pure Water Permeability Measurement with and without the Dolphin System.

Figure 2-6 shows permeate flow as a function of total volume filtered through the membrane for a 15 mg/L sodium alginate solution at pH 6.2. Permeate flow stays at about 90% of its initial value for the duration of the test when the Dolphin system is ON. When the solution is filtered with the Dolphin OFF, permeate flow falls to about 70% of the starting rate. These flow data indicate that sodium alginate behaves slightly differently

when exposed to an oscillating electromagnetic field, which appears to mitigate fouling to a modest extent.

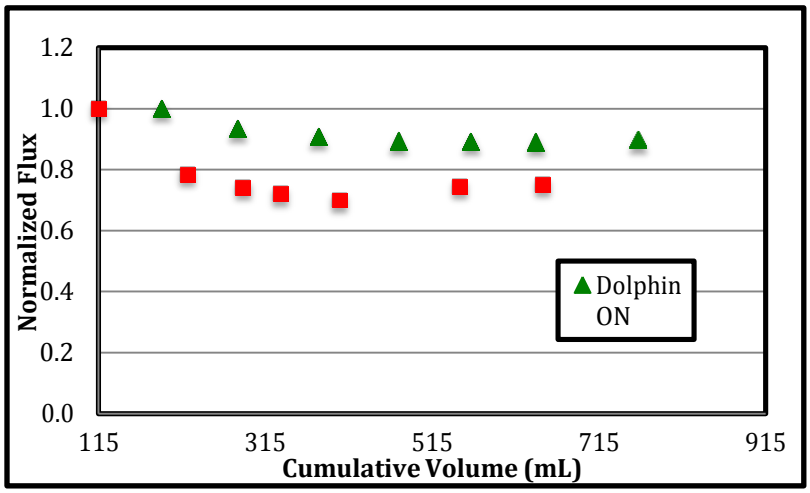


Figure 2-2. Effects of the Dolphin System during filtration of a 15mg/L sodium alginate solution in 10mM NaCl; Initial Flux: 330 LMH

Dextran solutions were prepared using dextran derived from *Leuconost mesenteroides*, a bacterium often involved in fermentation, with a molecular weight ranging from 100k to 200kDa. Figure 2-7 shows the fouling behavior of this model foulant as a function of cumulative volume. The difference between the filtration tests performed with and without the Dolphin system is negligible. Flux decline due to organic fouling falls to about 50% of the initial rate for both instances, resulting in the strongest case of fouling for the three model compounds. The rapid flux decline may be due to the size of the dextran molecules that accumulate on the surface of the 10kDa membrane.

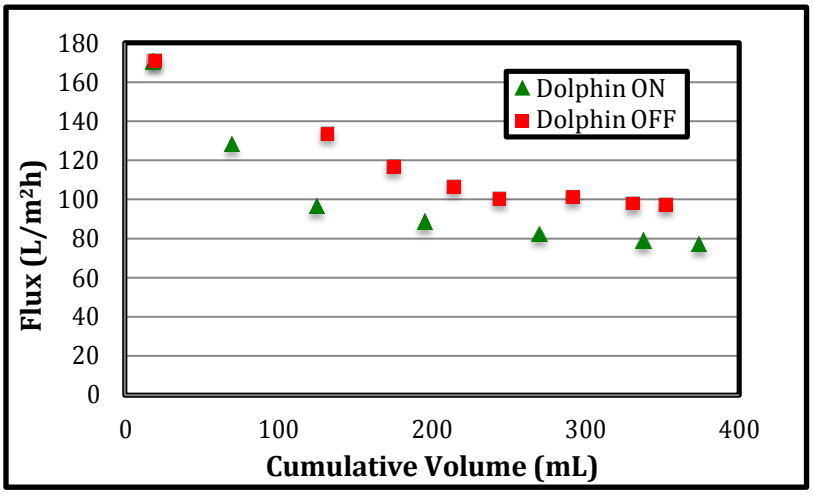


Figure 2-3. Effects of the Dolphin System during filtration of a 21 mg/L dextran solution in 10mM NaCl; Initial Flux: 170 LMH.

2.2.2 Biological Fouling

As a follow-up to the organic matter study, we investigated the effects of the Dolphin module during the filtration of a dilute bacterial suspension. A Biomax membrane with a molecular weight cutoff of 50 kDa was used to filter a *Pseudomonas putida* suspension. This bacterial solution was prepared using M9 media and glucose at a concentration of 1 g/mL. Optical density measurements were used to ensure that the bacterial population had reached exponential growth.

Figure 2-8 depicts flux decline as a function of time for the bacterial solution filtered on a 50kDa membrane at a pressure of 50psi. When the Dolphin system is activated there is a larger flux decline and after 2.5 hours of filtration, permeate flow falls to about 20% of the initial rate. This indicates that under these particular conditions, the Dolphin system affects the bacterial population in a way that results in stronger biofouling than when the feed solution is not exposed to the Dolphin module. Cells could be intact but stressed and they may produce extracellular material (polysaccharides or proteins) that could exacerbate fouling. Cells could also be lysed and internal cell components (proteins, etc) may be involved as foulants that can penetrate the membrane pore structure. The mechanisms responsible for these results are not completely understood but it has been accepted in the literature that disrupting bacterial cell membranes affects the way different biological components adhere to polymeric membrane surfaces.

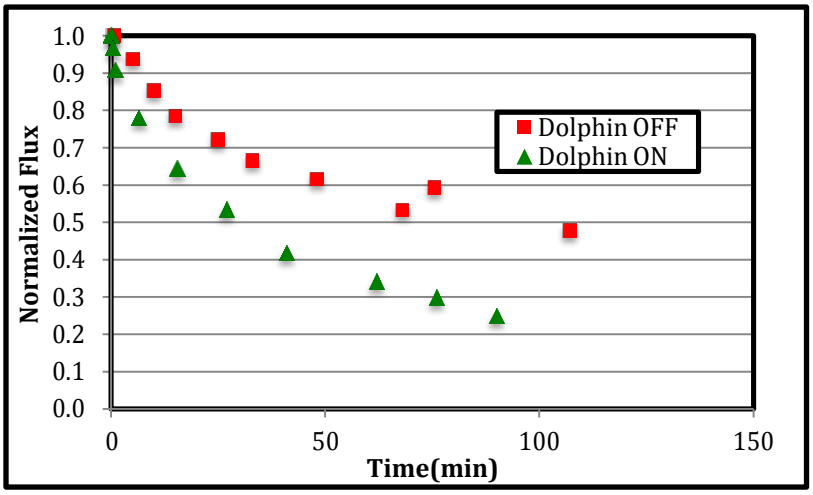


Figure 2-8. Effect of Dolphin System on the Permeate Flux during P. putida filtration using a 50kDa membrane (OD = 1.5).

2.2.3 Synthetic Flowback Solutions

Our focus up to this point had been evaluating the effects of pulsed electric fields on the way individual organic solutions interact with water treatment membranes. In an effort to gather further evidence on how the Dolphin system can be used during the pretreatment stage of flowback water, two synthetic solutions were prepared to simulate

the chemical composition and physical characteristics that are typically encountered in oil field operations. The first solution was an oil emulsion that contained heavy mineral oil at a concentration of 4 g/L, Aldrich humic acid at 156 mg/L, and NaCl at 1g/L. This model solution was kept at neutral pH and had a conductivity of 2080 μS/cm.

The flux curve for this synthetic solution is shown in Figure 2-9 during a 9-hour test using a 10 kDa polyethersulfone (PES) membrane. The overall flux reduction for both curves corresponds to approximately 50% of the initial rate. However, there is no visible difference in behavior between the filtration runs with and without the Dolphin system.

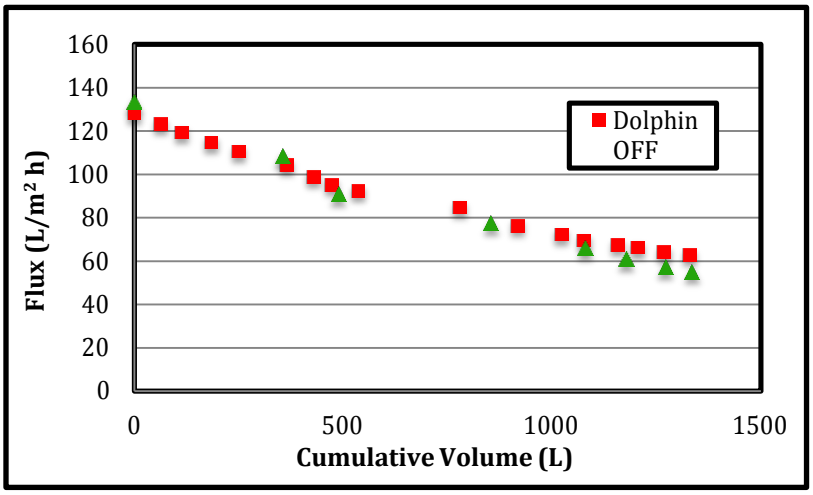


Figure 2-9. Oil emulsion flux measurements by cross-flow filtration for 10kDa PES membranes. Initial flux: 129 LMH.

A second synthetic solution was prepared with a more complex composition, including typical constituents of flowback water found in the literature. Table 2-2 summarizes these chemicals and their corresponding concentrations. Current literature on produced and flowback water indicates that the exact chemical composition is proprietary and can vary with location and time. There are certain additives that are not revealed as well as possible radioactive components that are difficult to detect. Table 2-2 contains the most commonly encountered components of flowback water (Gregory et al, 2011), assuming that pretreatment was provided to remove oil and propant (sand particles).

Table 2-2. Model Flowback Water Solution (pH 7)

Chemical Name	Concentration (g/L)	Purpose
Guar gum	10	Viscosity modifier
Strontium chloride	10	Metal
Barium sulfate	2	Metal
Manganese sulfate	0.1	Metal
n,n-imethylformamide	0.02	Corrosion inhibitor
Boric acid	0.01	Cross-linker
Isopropanol	10	Surfactant
Potassium chloride	10	Salt
Glutaraldehyde (20% soln)	0.01	Biocide
Calcium chloride	100	Hardness

Permeate flux curves are shown in Figure 2-10. The Dolphin system did not mitigate fouling; indeed, flux reduction is slightly greater when the Dolphin system is activated, although the difference is not significant.

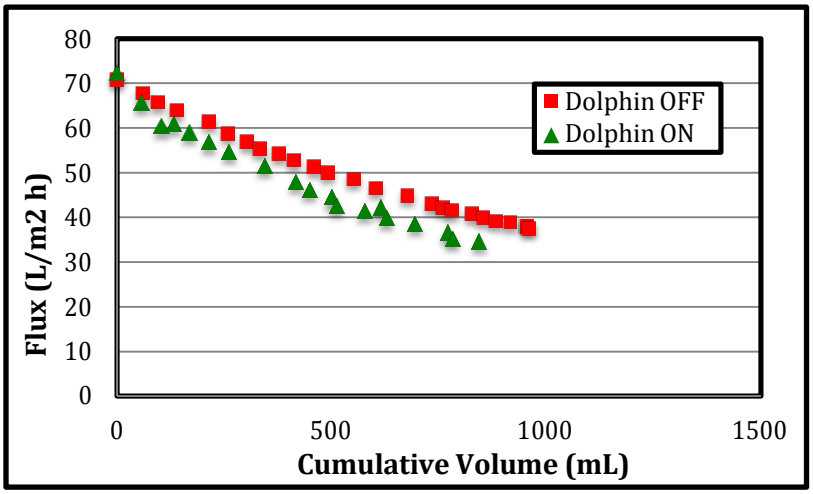


Figure 2-10. Synthetic Flowback water flux measurements by cross-flow filtration on a 10 kDa membrane. Initial Flux: 70 LMH.

Since the Dolphin system is currently being used in cooling towers to prevent scaling, corrosion, and biological fouling, we conduct a set of experiments to mimic typical cooling tower conditions. A solution containing 350 mg/L of $CaCO_3$, 10g/L of NaCl, and pH 8.5 was prepared and filtered through a nanofiltration (NF) membrane. An NF membrane was selected in this case to guarantee high salt rejection values with 100% recycling. Flux behavior of the scaling solution is shown in Figure 2-11. When the Dolphin system is ON, the permeate flux falls to about 45% of the initial value, whereas with the Dolphin the permeate flux falls to <35% of the initial value. The effect of the Dolphin system appears

significant, which is consistent with the cooling tower applications. Potential aggregation effects were investigated using dynamic light scattering measurements of the retentate stream. Samples from the retentate stream were collected towards the end of each test to estimate the particle size distribution of the water rejected by the nanofiltration membrane. Dynamic light scattering data were obtained using a Brookhaven 90Plus Particle Analyzer. Figures 2-12 and 2-13 show that when the Dolphin system is operating, the size distribution of particles in the retentate is shifted to larger diameters. This indicates that at high salt and hardness values the effects of the electromagnetic field induce aggregation and consequently lead to slower flux decline.

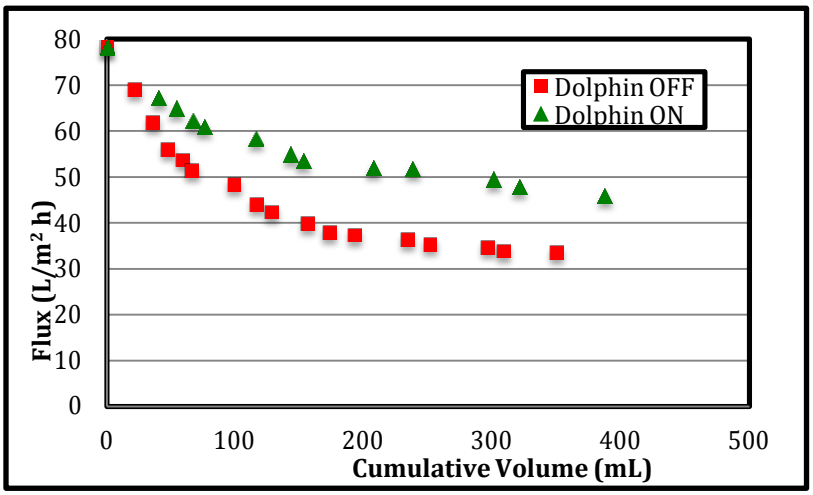


Figure 2-11. Scaling solution flux measurements by cross-flow filtration by a PES Nanofiltration membrane (>90% salt rejection). Initial flux: 79LMH.

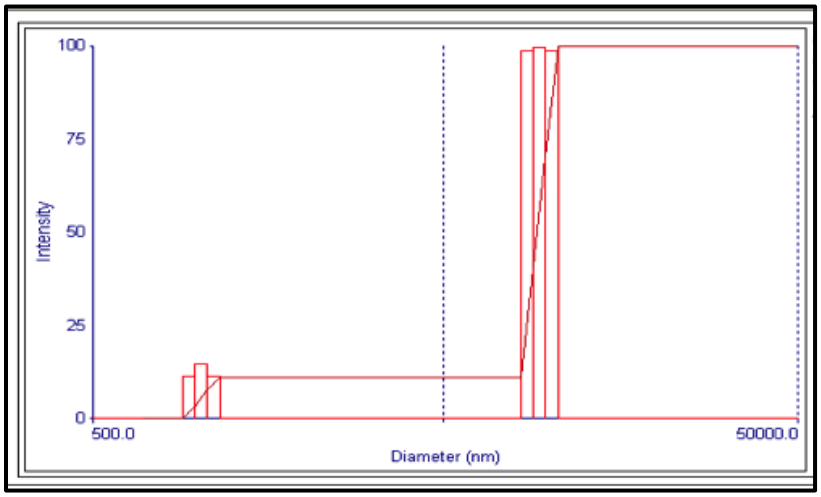


Figure 2-12. Dynamic Light Scattering data for the retentate stream of scaling solution from Figure 10. Dolphin ON

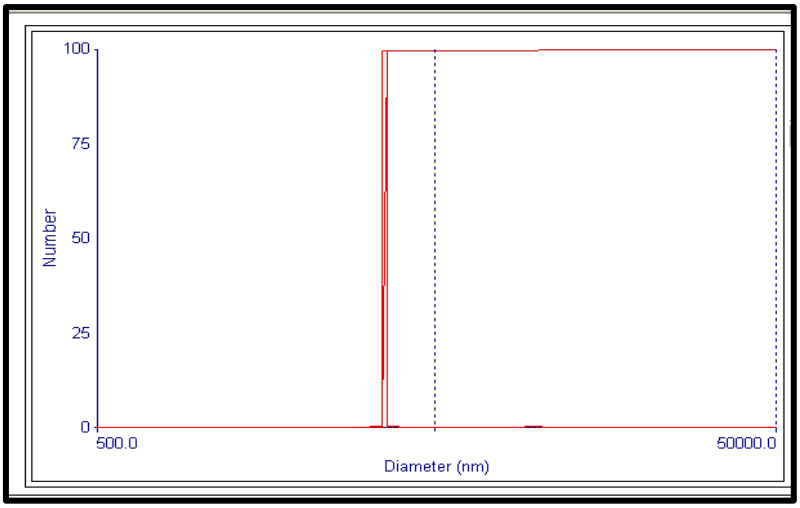


Figure 2-13. Dynamic Light Scattering data for the retentate stream of scaling solution from Figure 10. Dolphin OFF

2.2.4 Modeling to Identify Fouling Mechanisms

The flux decline date was analyzed using available fouling kinetics models to help determine whether the Dolphin system – the presence of an oscillating magnetic field – changes the fouling mechanism on polymeric membranes. There are three recognized fouling mechanisms for membrane filtration: pore blockage, pore constriction, and cake formation. These mechanisms take into account a reduction in the number of pores available for flow, a reduction in the pore diameter due to foulant adsorption, and the build-up of a cake on the surface of the membrane. Ho and Zydney developed a model that combines characteristics from pore blockage and cake formation. According to this model, total flow through the membrane at any time is governed by:

$$Q(t) = Q_o \left[\exp\left(-\frac{\alpha_b \Delta P C_F}{R_m} t \right) + \frac{R_m}{R_m + R_c} \left(1 - \exp\left(-\frac{\alpha_b \Delta P C_F}{R_m} t \right) \right) \right] \quad (2\text{-}1)$$

Where R_m is the clean membrane resistance, C_F is the average feed concentration, R_c is the flow resistance caused by the cake deposit, ΔP is the applied pressure, and α_b and α_c are rate parameters corresponding to pore blockage and cake formation. The flow resistance due to cake formation is given by:

$$R_c = \left(R_m + R_{c,o} \right) \sqrt{1 + \frac{2\alpha_c \Delta P C_b}{\left(R_m + R_{c,o} \right)^2} t} - R_m \quad (2\text{-}2)$$

The following lumped kinetic constants were defined:

$$k_b = \frac{\alpha_b \Delta P C_F}{R_m} \text{ and } k_c = \frac{2\alpha_c \Delta P C_F}{(R_m + R_{c,o})^2} \quad (2\text{-}3)$$

These two parameters, along with the initial resistance due to cake formation, $R_{c,o}$, and the initial flow through the membrane, Q_o, were varied simultaneously to minimize the sum of squared residuals (SSR) between the model and experimental values. Modeling parameters are tabulated in Table 2-3 for all filtration tests.

Table 1-3. Fouling Rate Constants.

			Rate Constants		
Feed Solution	**NaCl mM**	**Dolphin**	**Cake Formation, k_c (s^{-1})**	**Pore Blockage, k_b (s^{-1})**	**Membrane MWCO kDa**
Sodium Alginate	10	OFF	1.396E-04	0.00102	5
Sodium Alginate	10	ON	6.04E-05	0.00136	5
Sodium Alginate	50	OFF	6.55E-04	0.00151	5
Sodium Alginate	50	ON	5.80E-04	0.00139	5
S. River NOM	10	OFF	8.69E-05	0.00146	10
S. River NOM	10	ON	5.37E-05	0.00134	10
Aldrich Humic Acid	0	OFF	1.28E-03	0.00759	100
Aldrich Humic Acid	0	ON	9.102E-04	0.00602	100
Oil Emulsion	10 g/L	OFF	1.28E-04	0.00536	10
Oil Emulsion	10 g/L	ON	2.33E-04	0.00349	10
Synthetic Flowback		OFF	7.63E-05	0.0349	10
Synthetic Flowback		ON	1.17E-04	0.0349	10
Scaling Solution		OFF	2.40E-04	0.0520	NF
Scaling Solution		ON	1.00E-04	0.0520	NF

Plots of total resistance as a function of time were generated for each filtration experiment and the values of the kinetic constants for each fouling mechanism were evaluated. For most data sets, the cake formation rate constant was higher when the Dolphin system was not activated. This is likely due to the aggregation effects induced by the electromagnetic field. Resistance behavior due to Swannee River NOM fouling is shown in Figure 2-14 as a representative example. The filtration test performed with the Dolphin system results in slightly lower resistance values and slower rate for cake formation; the difference between the control and Dolphin curves seems to get greater as the filtration test evolves. However, the pore blockage parameters are similar. These trends were

observed for all organic solutions and for the scaling solution; it should be noted that higher ionic strength results in stronger fouling influence from cake formation.

Fouling effects due to filtration of an oil emulsion are shown in Figure 2-15. In this case, the total resistance is lower when the Dolphin system is activated but the cake formation rate constant is slightly higher than when the Dolphin is OFF. This was also observed for the synthetic flowback solution. This may be due to the complexity of these fouling solutions and the different interactions that may arise between the solutes and the membrane surface. If aggregation did occur, it may indicate an antagonistic effect of aggregation. For the flowback solution, the pore blockage rate constant was high than all other feeds, suggesting a different fouling mechanism.

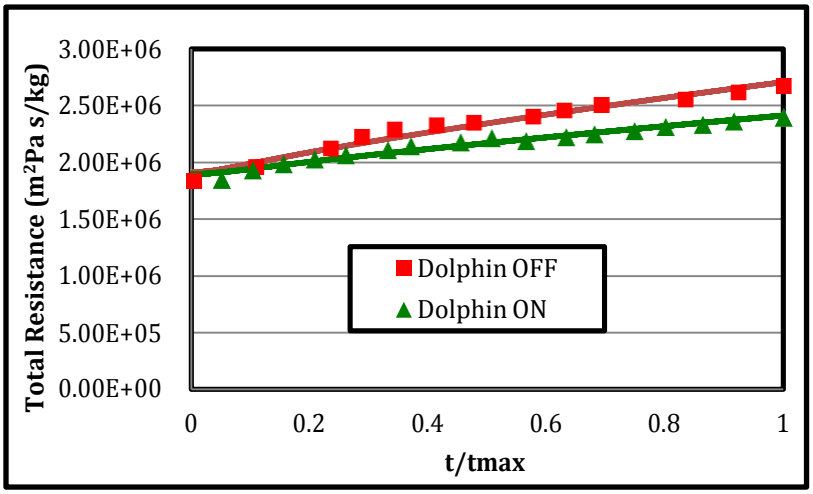


Figure 2-14. The effect of the Dolphin system on total resistance to Swannee River NOM filtration. Solid lines correspond to fits of the combined pore blockage-cake formation model.

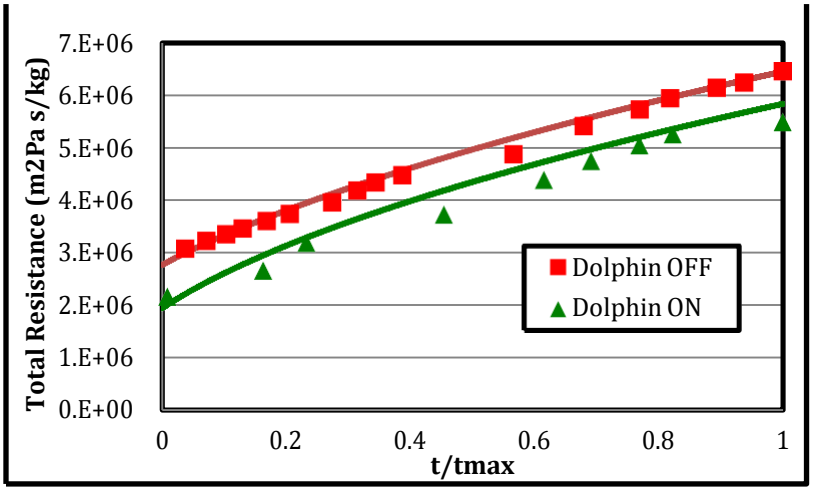


Figure 2-15. The effect of the Dolphin system on the total resistance due to filtration of oil emulsion. Solid lines correspond to fits of the combined fouling model.

3.0 Surface Modification to Mitigate Membrane Fouling

Surface modification using UV and plasma grafting techniques is known to help reduce fouling of ultrafiltration membranes. We seek to determine whether there is any positive synergy when the Dolphin system is used with modified surfaces. The Dolphin system may be effective in controlling fouling in modified surfaces that contain strong anti-fouling moieties.

We used atmospheric pressure (AP) plasma-induced graft polymerization as a modification method. This technique uses an AP plasma source where a beam of reactive ultra-pure Helium gas plasma is exposed to a 96-well plate with polyethersulfone (PES) membranes mounted and sealed at the bottom of each well. High throughput analysis was used to discover suitable monomers that could reduce the effects of fouling by an organic and synthetic flowback water solutions. This study revealed ideal chemical moieties that resist high salinity values and minimize fouling effects due to elevated solute concentrations. Monomers for the graft polymerization reactions were extracted from a library available from the high-throughput synthesis of protein-resistant surfaces. For this particular study, a total of 22 monomers were selected from a library of 66. These monomers belonged to three categories: amines, polyethylene glycols (PEG's), and basic & zwitterionic (right most column of Table 3 corresponds to formula weights). These three groups were selected based on data found on protein-resistant surfaces.

Table 2-1. Amine Monomers Used in Plasma Modification

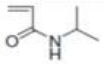
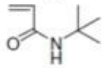
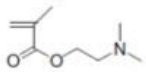
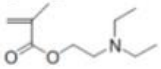
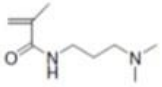
Amines				
N1	51	N-Isopropylacrylamide		113.16
N2*	52	N-tert-Butylacrylamide		127.18
N3	55	2-(Dimethylamino)ethyl methacrylate		157.21
N4*	56	2-(Diethylamino)ethyl methacrylate		185.26
N5	57	N-[3-(Dimethylamino)propyl]methacrylamide		170.25
N6	58	Acrylamide		71.08

Table 3-2. PEG Monomers Used in Plasma Modification

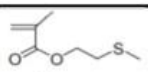
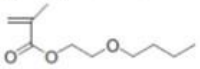
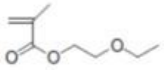
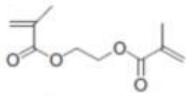
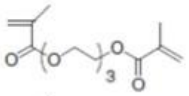
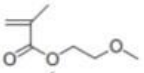
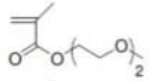
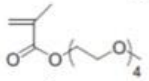
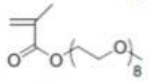
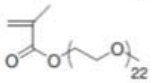
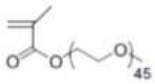
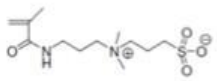
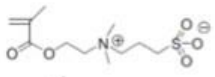
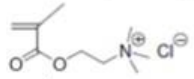
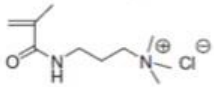
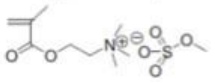
PEG's				
P1*	8	2-(Methylthio)ethyl methacrylate		160.23
P2*	12	2-Butoxyethyl methacrylate		186.25
P3*	23	2-Ethoxyethyl methacrylate		158.19
P4*	27	Ethylene glycol dimethacrylate		198.22
P5*	29	Triethylene glycol dimethacrylate		286.32
P6*	30	Ethylene glycol methyl ether methacrylate		144.17
P7*	31	Di(ethylene glycol) methyl ether methacrylate		188.22
P8	32	Poly(ethylene glycol) methyl ether methacrylate (n=4)		300
P9	33	Poly(ethylene glycol) methyl ether methacrylate (n=8)		475
P10	34	Poly(ethylene glycol) methyl ether methacrylate (n=22)		1100
P11	35	Poly(ethylene glycol) methyl ether methacrylate (n=45)		2080

Table 4-3. Basic & Zwitterionic Monomers Used in Plasma Modification

Basic and Zwitterionic				
B1	59	[3-(Methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide inner salt		292.39
B2	60	[2-(Methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide		279.35
B3	61	[2-(Methacryloyloxy)ethyl] trimethylammonium chloride		207.70
B4	62	[3-(Methacryloylamino)propyl] trimethylammonium chloride		220.74
B5	63	[2-(Methacryloyloxy)ethyl] trimethylammonium methyl sulfate		283.34

Two 96-well plates containing 100kDa PES membranes were modified using the atmospheric plasma technique. Pure water filtration was measured the day after modification using a multi-well plate vacuum manifold at a transmembrane pressure (TMP) of 68kPa. Permeate volume was collected in a 96-well receiver plate and a microplate spectrophotometer (PowerWave, BioTek Instruments, Inc.) was used to measure absorbance at 977 nm; where volume was subsequently obtained from calibrated measurements. Permeate flux was calculated using a well area of 1.995×10^{-5} m^2 and a filtration time of 120 seconds. Fouling effects were estimated by comparing resistance values prior to and after a 48-hour static fouling test. Fouling effects were quantified by the fouling index, defined as the ratio of the resistance difference between the fouled and unfouled membranes for the modified and control (unmodified) membranes:

$$\Re = \frac{\left(R_{fouled} - R_{unfouled}\right)^{\text{modified}}}{\left(R_{fouled} - R_{unfouled}\right)_{\text{control}}} \qquad (3\text{-}1)$$

Two fouling solutions were prepared for this part of the study. The first was an organic solution containing 40 mg/L sodium alginate and 10 mM NaCl at a pH of 6.3. The second solution contained all the chemicals listed in Table 2-2 at their designated concentrations and with a pH of 7.9. At the beginning of each fouling test, 200 μL of solution were added to all 96 wells and left undisturbed for 2 days. At the end of the cycle, the fouling solutions were discarded and pure water permeability was measured and compared to the values obtained prior to the test.

In order to select the monomers that resulted in low fouling conditions, a plot of fouling index vs. normalized resistance was generated for each case. An error of 5% was calculated based on standard deviation values obtained from absorbance measurements. A fouling index lower than 1 indicates that surface modification results in a material that is foulant-resistant as compared to the as-received control. Figure 3-1 shows that P6, N3, B2, and B5 can be selected as promising monomers that lead to lower interactions between the solutes and the membrane surface, resulting in minimal fouling. Basic & zwitterionic moieties seem to have the greatest positive effect on fouling reduction highly due to the presence of positive and negative charges. These findings are consistent with the work done by Zhou et al. (2005) and Zhou (2009) on NOM fouling and UV polymerization of water treatment membranes.

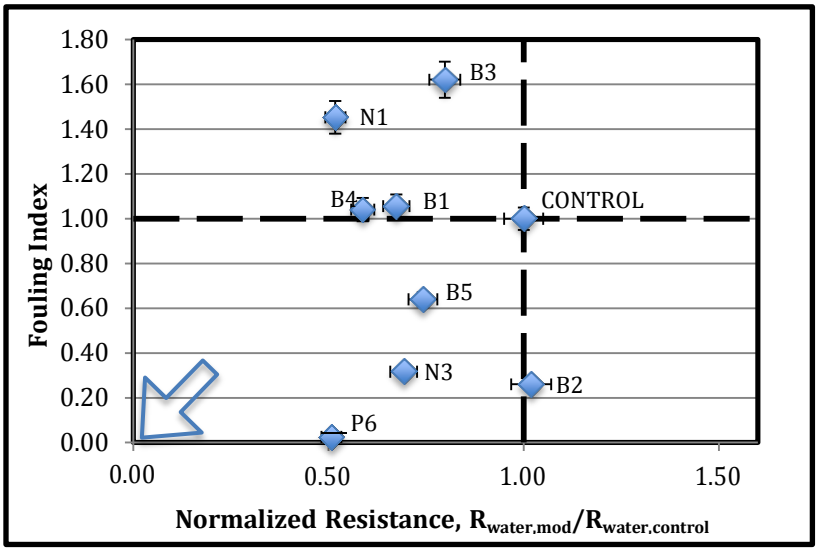


Figure 3-1. Effects of surface modification on organic fouling – 40 mg/L Sodium alginate solution; pH 6.3

The second fouling test involved our previously used synthetic flowback water solution to test how changes in surface chemistry could lead to lower fouling effects. In general, static fouling effects caused by our model flowback solution led to fouling indices that were higher than most of those shown in Figure 3-1. Most of the monomers used during plasma modification resulted in either higher flow resistance or would lead to fouling characteristics that were worse than the unmodified case. However, as seen in Figure 3-2, modification with monomers P3, B4 and B5 corresponded to low fouling and overall resistance. We see once again that basic & zwitterionic compounds contribute positively to fouling reduction even if the foulant is a complex solution.

Surface modification of polymeric membranes can lead to the discovery of novel materials that are resistant to fouling and could therefore lead to sustained production rates, lower energy costs, and reduced chemical and surfactant usage. The information gathered during these two static fouling tests suggests promising alternative solutions to dynamic fouling focusing primarily on surface chemistry.

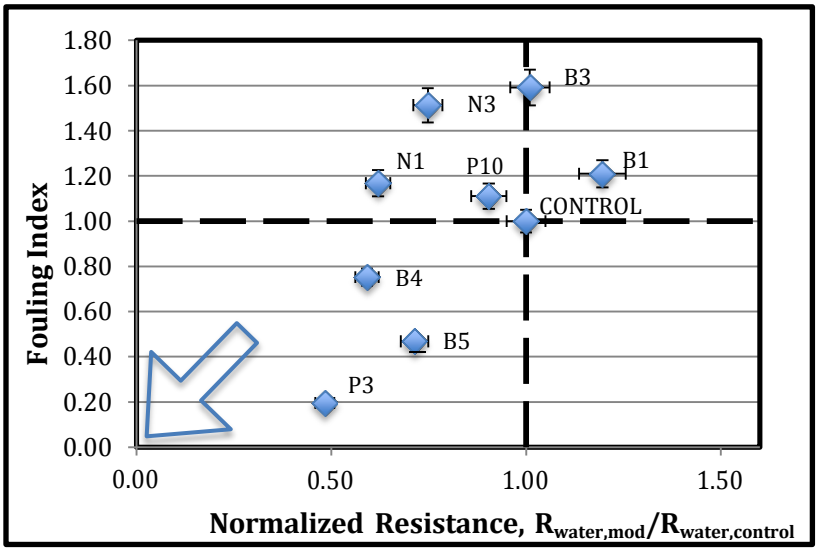


Figure 3-2. Effects of surface modification on fouling by synthetic flowback water.

4.0 Biofilm Formation

4.1 Biofilm Drip Reactor and Evaluaiton of Gallium Chloride

We have also been studying biofilm formation on surfaces under varying chemical and physical conditions. Our first study involved a metal-reducing bacterium, *Shewanella oneidensis* MR-1, known to produce a strong biofilm that enables electron transfer from the medium to its outer membrane. We are currently using Fe(III) nitrilotriacetic acid (Fe NTA) and $GaCl_3$ – dissolved electron acceptors – to observe biofilm growth on glass slides. Bacteria were inoculated onto the biofilm drip reactor shown in Figure 4-1 and then fed a chemically defined medium composed of salts, minerals, vitamins and amino acids. Lactic acid was used as the primary electron donor (carbon source) in the system.

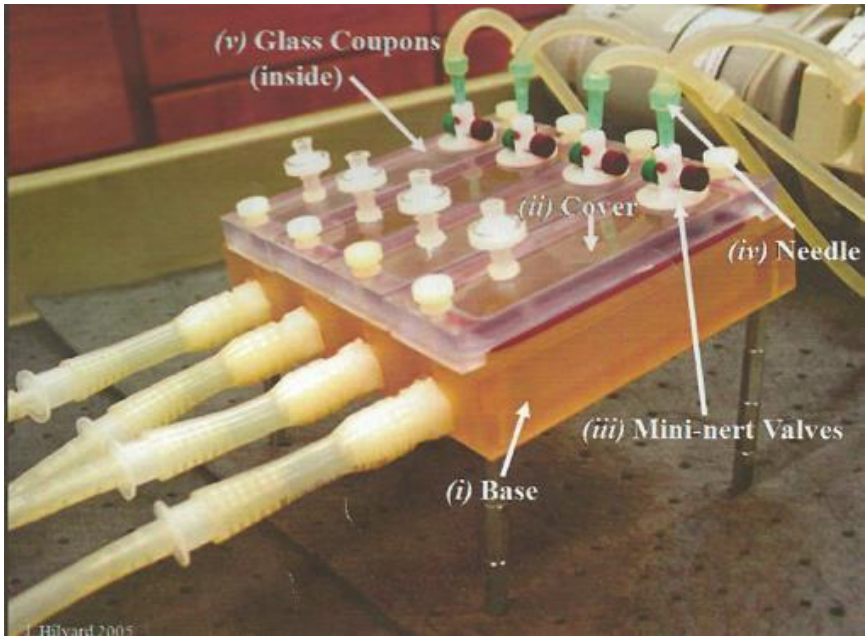
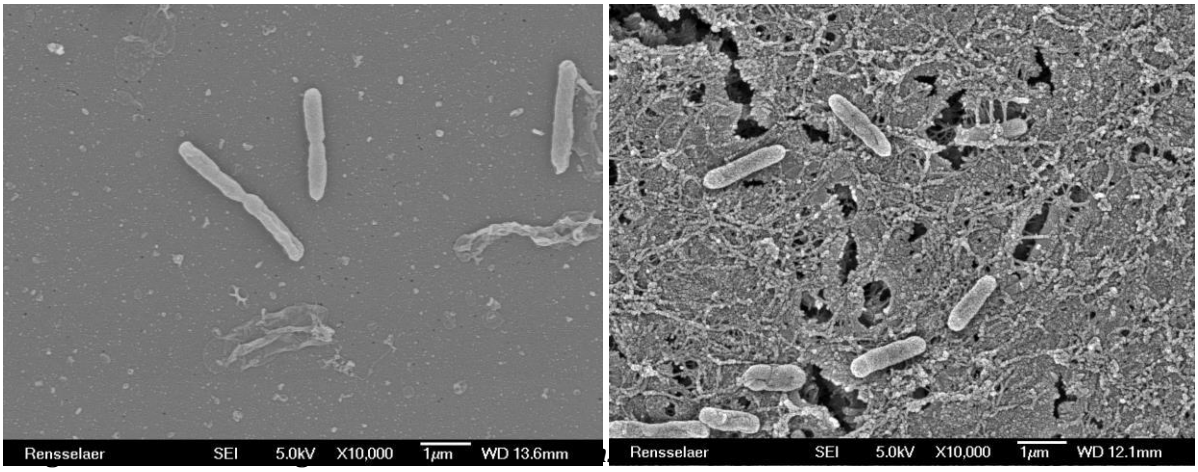


Figure 4-1. Biofilm Drip Reactor.

The first round of tests was designed to collect data on the effects of gallium chloride on biofilm growth. Two compartments in the drip reactor received a feeding solution with 30μM of Fe NTA, while the other two contained 30μM $GaCl_3$ in the nutrient medium. The test was conducted for 6 days and the glass slides were fixed and prepared for scanning electron imaging (SEM). These results are shown in Figure 4-2.



(left) and $GaCl_3$ (right).

The image on the left of Figure 4-2 corresponds to a biofilm grown with nutrient medium that contained dissolved Fe NTA. This micrograph shows a dense biofilm with significant production of extra polysaccharides and a seemingly stable bacterial population. The image on the right, was fed with a gallium chloride medium, depicts a weak and dispersed biofilm that lacks extrapolymeric substances. These results indicate that gallium chloride is an inhibitor of biofilm growth.

Biological fouling is one of the most persistent operational problems in membrane treatment plants. Our goal is to develop strategies that minimize biofilm growth on polymeric membranes and improve the productivity and sustainability of membrane systems. Gallium chloride seems to be a promising and novel biocide for such purposes.

5.1 Modeling Solute Transport

In this section, we present work done toward development of a transport model to quantify rejection of organic constituents present in flowback water by nanofiltration membranes. We incorporate the effects of adsorption, a novel feature of this work.

5.1 Introduction

Applications of membrane technologies for water purification have been expanding significantly. Membranes are classified according to their pore size, separation mechanism, and mode of operation. Microfiltration (MF) membranes have the largest pores; they are capable of removing particulates and controlling turbidity via a size exclusion (sieving) mechanism. Ultrafiltration (UF) membranes have macromolecular-sized pores and can provide protection from pathogenic microorganisms (including protozoans, bacteria, and viruses) and partially remove natural dissolved organic matter (NOM) via a combination of size and charge; the effect of charge is greatest when the molecule size approaches that of the pore. RO membranes do not have pores and are capable of desalination via selective solute solubility and permeability (solution/diffusion) in the membrane polymer matrix. The behavior of nanofiltration (NF) membranes falls between that of UF and RO membranes. Typical NF membrane molecular weight cut-off (MWCO) values, which define the molecular mass of the largest solute capable of passing through the membrane, are in the range of 300 to 1000 Daltons. The effects of both solute size and charge play an important role in solute transport and rejection. NF membranes were originally developed for membrane softening of hard groundwater because of their ability to reject divalent cations, and are now widely used to remove salts (from brackish water), hardness, and natural organic matter (NOM). While MF membranes can be operated in either dead-end flow or cross-flow, UF, NF, and RO systems are run in cross-flow mode in order to minimize fouling. The salient characteristics of these different membranes are shown in Table 5-1.

Table 5-1: Membrane Characteristics

Type	Pore Size [nm]	Molecular weight Cutoff [Da]	Operating Pressure [PSI]	Removal Target
Microfiltration	>100	NA[2]	5-30	Particulates, colloids, microbes
Ultrafiltration	2 to 100	1,000 to 500,000	10-100	virus, macromolecules[3]
Nanofiltration	1 to 2	200 to 1,000	75-150	Divalent ions, organics
Reverse Osmosis	NA[1]	<200	150-2,000	Monovalent ions

Notes: [1]Reverse osmosis membranes do not have true pores; it is thought that transport occurs through polymer free volume. [2]Microfiltration membranes remove particulates, therefore it is not appropriate to express in terms of molecular weight. [3]Macromolecules include natural organic matter and proteins.

During nanofiltration, solutes are rejected by a combination of steric (size) exclusion and charge exclusion, also called Donnan exclusion. In addition, solute

adsorption may also play a role. To understand these processes, research has been conducted to evaluate the transport of hormones (Nghiem and Schafer, 2002; Nghiem et al., 2002; Nghiem et al., 2004a; Nghiem et al., 2004b; Schafer et al., 2003); pesticides and other organics (Van der Bruggen et al., 1998; Van der Bruggen et al., 1999; Van der Bruggen et al., 2001; Van der Bruggen and Vandecasteele, 2001; Van der Bruggen et al., 2002; Van der Bruggen and Vandecasteele, 2002; Zhang et al., 2004); and neutral endocrine disrupting compounds and pharmaceutical active compounds (Kiso et al., 1992; Kiso et al., 1999a; Kiso et al., 1999b; Kiso et al., 2001; Kiso et al. 2002).

Factors influencing transport include molecular size, polarity, charge, and hydrophobicity (Kimura et al., 2003; Kimura et al., 2004). It has been shown that hydrophobic compounds adsorb onto membranes to some extent and lead to flux decline during filtration. In some cases, this adsorption can result in an overestimation of rejection (Kimura et al., 2003). Recently, the use of membranes as an adsorbent medium (membrane adsorber) has been developed to separate proteins(Avramescu et al., 2003a,b); endotoxins(Avramescu et al., 2003c), and small inorganic molecules (Hradil et al., 2004).

Although organic solutes can be removed by membrane adsorption the adsorption capacity of membranes is usually small, and equilibrium (saturation will be reached quickly during filtration. After the membrane is saturated with solute, adsorption no longer occurs. Therefore, to predict how permeate concentration changes during filtration, to prevent the overestimation of the rejection, and to correctly interpret transport parameters, it is necessary to have a model that captures the behavior of solute transport as a function of time, the "breakthrough" behavior.

Several mechanistic and mathematical models are currently available to describe mass transfer through NF or RO membranes. Williams evaluated the modified solution-diffusion model for steady-state transport and diffusion-adsorption model for transient (unsteady state) concentration profiles (Williams et al., 1999). These two models need to be numerically solved and they could not predict concentration profiles very well. Other models are developed for the prediction of organic retention as a function of molecular weight (Nghiem et al., 2004; Zhang et al., 2004), a function of transmembrane pressure (Wendler et al., 2002), or a function of flux (Wang et al, 1997). These models could only describe or predict solute transport at steady state, after the transient breakthrough stage.

A simple approach is to use a solute flux expression based on the solution diffusion model, which assumes that diffusion dominates transport, and solute coupling is negligible:

$$J_s = J_v C_p = k_s (C_w - C_p) \qquad (5\text{-}1)$$

where J_s is the average solute flux (mol/m^{2}s), J_v is the volumetric solution flux (m/s), C_w and C_p are the solute concentrations at the membrane surface ("wall") and in the permeate, respectively, and k_s is the solute permeation coefficient, related to the solute diffusivity,

solute partition coefficient in the membrane, and the membrane thickness. Here, $C_w - C_p$ is the driving force for diffusion across the membrane.

Another approach to modeling solute transport is to account for a combination of convection and diffusion. Diffusion is accounted for in terms of an infinite dilution diffusion coefficient, D_L (m^2/s), and the concentration gradient in the pore. Both diffusion and convection are hindered relative to their bulk values when the solute size approaches the pore size, which is accounted for by hindrance factors for diffusion, K_d, and convection, K_c:

$$J_s = -K_d D_L \frac{dC}{dx} + K_c J_v C \qquad (5\text{-}2)$$

One-dimensional solute transport through macroscopic porous media is well developed and has been used in many systems, especially contaminant transport in soils or soil beds (Lapidus and Amundson, 1952; Brenner, 1962; Lindstrom et al., 1967; Van Genuchten and Parker, 1984; Leij et al., 1991; Prince et al., 2000). Although the geometry is different, membranes are also porous media, with nano-scale pores. Therefore, the one-D porous medium model may be a suitable starting point for modeling solute transport through membranes. In comparison to macroscopic porous media, transport of a solute through nanometer sized pores not much bigger than the solute itself results in hindered or restricted transport (Deen et al., 1981; Deen, 1987; Davidson and Deen, 1988; Bowen and Sharif, 1994; Schaep et al., 1999). As a consequence, the solute apparent diffusion coefficient is much lower than in bulk solution, and rate of convective transport of the solute is lower than the product of bulk concentration and volume flow rate, a phenomenon discussed by Deen (1987).

This study aimed at describing the permeate breakthrough behavior of the organic compounds nanofiltration process using one-dimensional solute transport through porous medium model coupled with the hindered transport theory. Our anticipated outcome is that by modeling the process, organic solute removal mechanisms will be understood more thoroughly, which will lead to better understanding of how organic additives in frac water are removed.

5.2 Theory

5.2.1 One-D solute transport through porous media model

Steady State Model. The steady-state model has been derived from the expanded Nernst-Plank equation (Lueptow and Lee, 2001) with electrostatic repulsion ignored. Integrating the convection-diffusion solute flux expression (Eq. 5-2) across the membrane thickness yields:

$$S_m = \frac{S_\infty \exp(N_{Pe})}{S_\infty + \exp(N_{Pe}) - 1} \tag{5-3}$$

where the "sieving coefficient" $S_m = C_p/C_m$ is expressed in terms of an asymptotic sieving coefficient, S_∞, and the membrane Peclet number. The Peclet number is based on the pore velocity, J_v/ε, and a characteristic length equal to the membrane thickness, δ_m:

$$N_{Pe} = \frac{J_v \delta_m \Phi K_c}{D_L \varepsilon \Phi K_d} \tag{5-4}$$

where ε is the membrane porosity and K_c and K_d are hindrance factors based on the ratio of the solute to membrane diameter, and the membrane charge density. The partition coefficient Φ expresses the difference in the bulk concentration and the pore concentration at equilibrium; these may be different as a result of packing efficiency. Equation (5-3) indicates that when convection is zero, the sieving coefficient goes to 1 and rejection goes to zero because the feed equilibrates with the permeate via diffusion. As convection increases, the sieving coefficient decreases and rejection increases, because the solvent flux becomes greater than the solute flux, essentially "diluting" the permeate. In the limit of infinite convection, the sieving coefficient reaches its asymptotic (minimum) value, S_∞.

It should be noted that an important criterion for a dynamic model is agreement with the steady-state model as time approaches to infinity. In this study, the time for the dynamic model to meet steady state primarily depends on the amount of adsorption.

5.2.2 Convection-diffusion-adsorption equation

The well-known mass conservation equation for one-dimensional solute transport, which is also called advection-diffusion-adsorption equation, can be written as:

$$\frac{\partial C}{\partial t} = -v^* \frac{\partial C}{\partial x} + D^* \frac{\partial^2 C}{\partial x^2} - \frac{\rho}{\varepsilon} \frac{\partial q}{\partial t} \tag{5-5}$$

C is the cross-section averaged liquid phase concentration (mol/m^3), t is the time (s), x is the position in medium in the fluid moving direction (m), v^* is the hindered solute velocity in the membrane pores (m/s), D^* is the hindered solute diffusion coefficient (m^2/s), ρ is the porous medium solid bulk density (kg/m^3), ε is the medium porosity, q is amount of solute absorbed by per unit weight of porous medium (mol of solute/kg of adsorbent).

In order to solve the equation analytically, two assumptions are normally made: local equilibrium and linear isotherm. Local equilibrium assumption indicates that at any position, the bulk liquid phase and the solid phase are in equilibrium; this implies no mass transfer limitation controlling the rate of adsorption. Expanding the time rate of adsorption term yields:

$$\frac{\partial q}{\partial t} = \frac{\partial q}{\partial C}\frac{\partial C}{\partial t} \tag{5-6}$$

Under the local equilibrium assumption, the $\partial q/\partial C$ term can be obtained directly from the adsorption isotherm, i.e., $\partial q/\partial C = \partial q_e/\partial C_e$. If the isotherm is linear, then $\partial q_e/\partial C_e = K_D$, the linear partition coefficient. Substituting back into Eq. (5-5) and rearranging yields:

$$R\frac{\partial C}{\partial t} = -v^*\frac{\partial C}{\partial x} + D^*\frac{\partial^2 C}{\partial x^2} \quad \text{where } R = 1 + \frac{\rho}{\varepsilon}K_D \tag{5-7}$$

Where R is called the retardation factor, which accounts for linear and reversible equilibrium adsorption. If $R = 1$, no sorption occurs. With the appropriate boundary condition (discussed below), the analytical solution is as follows:

$$\frac{C_p(t)}{C_b} = \frac{1}{2}erfc\left[\frac{RL - v^*t}{2(D^*Rt)^{1/2}}\right] + \frac{1}{2}\exp\left(\frac{v^*L}{D^*}\right)erfc\left[\frac{RL + v^*t}{2(D^*Rt)^{1/2}}\right] \tag{5-8}$$

Where C_b is feed bulk solute concentration (mol/m^3), C_p is permeate concentration (mol/m^3), and L is porous medium effective thickness (m). If the solute adsorption is described by a non-linear isotherm, the PDE (Eq. 5-5) becomes non-linear. In this study, the adsorption isotherm (data is shown in following sections) can be described by Freundlich equation. In the isotherm experiment, the equilibrium concentration was measured in the bulk; this can be related to the pore concentration using the partition or distribution coefficient, Φ:

$$q_e = K_F C_{e,bulk}^n = K_F\left(\frac{C_e}{\Phi}\right)^n \tag{5-9}$$

Taking the derivative, $\partial q_e/\partial C_e = (K_F/\Phi^n)n(C_e)^{n-1}$ and now R depends on concentration. Substituting back into Eq. (5) and rearranging yields:

$$\left(1 + \frac{\rho}{\varepsilon}K_F\frac{nC^{n-1}}{\Phi^n}\right)\frac{\partial C}{\partial t} = -v^*\frac{\partial C}{\partial x} + D^*\frac{\partial^2 C}{\partial x^2} \tag{5-10}$$

This equation cannot be solved analytically and therefore must be solved numerically.

5.2.3 Boundary conditions

In the study of steady state transport of membrane, a flux-type of model has been used to estimate the permeate concentration and concentration profile through the membrane (Leuptow and Lee, 2001). In this case, as mentioned before, in order to keep in agreement with the steady-state model former developed, the boundary conditions are developed with the full understanding of the derivation from expanded Nernst-Plank

equation to the steady-state model. The boundary conditions and initial condition are as following:

$$\begin{cases} \left[-D^* \dfrac{\partial C}{\partial x} + v^* C \right](L,t) = vC_p \\ \dfrac{C(0,t)}{C_w} = \dfrac{C(L,t)}{C_p} = \Phi \\ C(x,0) = 0 \end{cases} \tag{5-11}$$

Where C_w is the concentration of the solute outside the pores at the inlet. Normally C_w is higher than the bulk feed concentration, because of concentration polarization, but in this study, since a high mixing rate was applied, they are nearly equal. Some studies used similar boundary conditions, but set $C_w = KC(0, t)$, and $C_p = C(L,t)$ yielding the following boundary condition at the inlet:

$$\left[-D^* \frac{\partial C}{\partial x} + v^* C \right](0,t) = v^* KC_w \tag{5-12}$$

The K here is also referred as a partition coefficient, but it is regarded as a result of combination of different effects. Such boundary conditions can successfully describe the change of concentration polarization and permeate concentration over time. But this boundary condition seems to result in a flat concentration profile across the membrane, which is inconsistent with the widely accepted opinion that the profile should have a slope. In this study, the nonlinear equation with the boundary conditions we developed has been studied by numerical method.

5.2.4 Hindered transport theory

To investigate the hindered transport, the membrane can be considered as an array of cylindrical tubes (pores) having the same radius. The characteristic radii of the solute and pores are assumed to be comparable to one another but much larger than that of the solvent. Mathematically, the hindrance effect on an uncharged, solid, spherical solute diffusion and convection in the pores can be considered by applying two hydrodynamic hindrance factors, K_d and K_c, to the diffusion and convection term, respectively, as discussed above (Eq. 5-2). Many equations are available in the literature to calculate the hydrodynamic coefficients K_d and K_c, and all of them correlated these two parameters with a function of the solute-to-pore size ratio $\lambda = r_s/r_p$. Expressions given by Bungay and Brenner (1973) are valid for $0 \le \lambda < 1$, and are chosen in this study:

$$K_d = \frac{6\pi}{K_t} \tag{5-13a}$$

$$K_c = \frac{(2-\Phi)K_s}{2K_t} \tag{5-13b}$$

where

$$K_t = \frac{9}{4}p^2\sqrt{2}(1-\lambda)^{-5/2}\left[1+\sum_{n=1}^{4}a_n(1-\lambda)^n\right]+\sum_{n=3}^{n}a_n(1-\lambda)^n \tag{5-13c}$$

$$K_s = \frac{9}{4}\pi^2\sqrt{2}(1-\lambda)^{-5/2}\left[1+\sum_{n=1}^{4}b_n(1-\lambda)^n\right]+\sum_{n=3}^{n}b_n(1-\lambda)^n \tag{5-13d}$$

The coefficients a_n and b_n in this equation can be found in the literature (Bungay and Brenner 1973). For hard-sphere particles where only steric interactions are considered, the partition (or distribution) coefficient is given by :

$$\Phi = \frac{C_0}{C_b} = \frac{C_L}{C_f} = (1-\lambda)^2 \tag{5-14}$$

Where C_o and C_L are solute concentrations just inside of the pore at the entrance and exit (mol/m^3). The relationships between hindrance factors and the solute to pore size ratio are shown in **Figure 5-1**. When solute moves along the cylindrical pores, the wall effect increases hydrodynamic drag on the solute relative to that in an unbounded fluid, which lowers the effective diffusivity relative to the value in bulk solution (K_d < 1). As for convection, the pore wall effect makes the solute more likely to travel along the pore centerline, the region of greatest accessibility to a large solute. Because the pore length is much larger than the pore radius, the fluid velocity is well developed in the pores, and shows a parabolic profile. Based on a well-developed parabolic fluid profile, the local solution velocity at the centerline is equal to twice the average velocity through the pore. When the flux through the pore is expressed in terms of the area-average solution velocity and the area-average solute concentration, the effective solute velocity is thus greater than the solution velocity (K_c > 1).

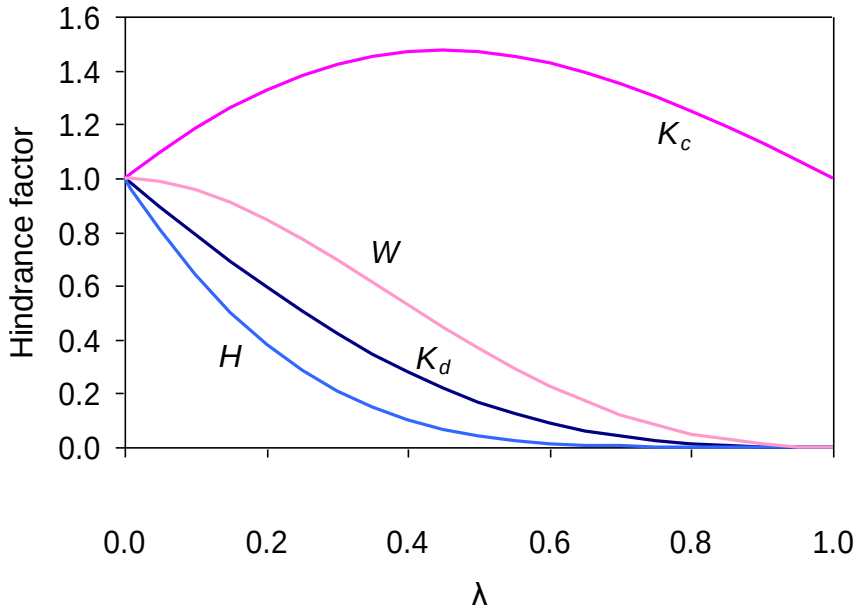


Figure 5-1. Dependence of hindrance factors for diffusion (Kd, H) and convection (Kc, W) of a neutral, spherical solute on the ratio of solute size to pore size, l. Functions H = ΦKd and W = ΦKc are also shown.

5.2.5 Determination of parameters

Membrane effective thickness L was measured in the lab with a SEM (Field Emission Scanning Electron Microscope, Joel JSM-6330F). Pore radii data r_p for all three membranes were obtained from the literature. Average membrane porosity ε was calculated based on membrane effective thickness and pore radius, using the equation:

$$L_p = \frac{\varepsilon r_p^{\,2}}{8\eta L} \qquad (5\text{-}15)$$

where η is the solution viscosity (kg/m·s), L_p is membrane permeability, which is the slope of DI water flux versus operating pressure. The solute radius r_s can be related to the diffusion coefficient of a solute in an infinitely dilute bulk solution D_L using the Stokes-Einstein equation:

$$D_L = \frac{kT}{6\pi\eta r_s} \qquad (5\text{-}16)$$

where k is Boltzmann's constant (1.38×10^{-23} J/K or kg m^2/s^2 K), T is absolute temperature (K), μ is the solvent viscosity (kg/m·s), and r_s is the hydrodynamic radius of the solute (m). The bulk solution diffusion coefficient under infinite dilution conditions were calculated using the Wilke-Change correlation (Cussler, 1997). The solution superficial velocity, v_s, is

equal to the membrane permeate flux. Then unperturbed fluid velocity in pores, v, was calculated based on membrane porosity and superficial velocity v_s by the relation $v = v_s/\varepsilon$.

5.3. Experimental and Numerical Methods

5.3.1 Materials

Three nanofiltration membranes were used in this research. The NTR 7450, (Nitto Denko, Inc., Japan) is made of sulfonated polyethersulfone whereas the NF 90 and NF 270 (Dow Filmtech) are aromatic polyamide thin-film composite membranes. Membrane properties are shown in Table 5-2.

The organic chemicals used in this study were phenol and 2,4-Dinitrophenol (DNP) purchased from fisher Scientific and Acros Organics, respectively. Molecular properties are shown in Table 5-3. Phenol and 2,4-dinitrophenol were chosen for membrane transport experiments as model aromatic organic compounds. It is thought that the ring structure may present some favorable interactions with membrane polymers structures (e.g., poly(ether sulfone) and aromatic poly(amide) materials). In addition, they have relatively low Henry's constants, indicating that they are not very volatile substances. This increases the accuracy of experiments by minimizing transfer into the gas phase and eliminating the need for headspace -free operation. While they compounds are expected to exhibit sorption interactions, they are not extremely hydrophobic, as indicated by their modest log octanol-water partition coefficients (log K_{ow}). For comparison, naphthalene and benzene possess log K_{ow} values of 3.3 and 2.13 respectively. This indicates that adsorptive losses to system components other than the membranes should be small. Finally, their solubility can be manipulated by changing their speciation as a function of pH. Stock solutions were made using these chemicals and DI water, and then stored in the refrigerator at 4 °C. Right before filtration experiments, stock solutions were diluted with DI water to around 0.002 mol/l for phenol and 0.0001 mol/l for 2,4-DNP. After dilution, no additional species were added into solutions. The pH of phenol and 2,4-DNP solutions was 6.10 and 4.30 respectively. The concentrations were measured by the Agilent 1100 HPLC system.

Table 5-2. Membrane Properties

Parameter	NTR 7450	NF 90	NF 270
Hydraulic permeability, L_p (LMH/psi)	0.581	0.642	0.875
Pore radius, r_p (nm)	0.80[1]	0.55[2]	0.71[2]
Skin thickness, L (μm)	0.91	0.25	0.36
Membrane porosity	0.203	0.273	0.168

Notes: data from [1]Hilal et al., 2005; [2]Schaep et al., 1998.

Table 3. – Adsorbate Properties

Compound	Formula	MW [g/mol]	Solubility [mg/L], 25 C	log Kow [-]	Pi energy [□]	Refractivity $10^6 \cdot [m^3 \cdot mol^{-1}]$	Polarizability $(Å)^3$
Phenol	C_6H_5OH	94.11	82.800	1.46	12.31	28.04	9.81
2,4-dinitrophenol	$C_6H_3(NO_2)_2OH$	184.11	2,790	1.67	34.10	42.69	14.11

Notes: Solubility and log (octanol water partition coefficient) (log K_{ow}) values were obtained from EPI Suite software (U.S. Environmental Protection Agency); reported experimental database values are shown. Pi energy values calculated from the Hückel molecular orbital theory using ChemAxon software. Refractivity values calculated using the atomic contribution method of Viswanadhan et al. (1989) as implemented in the ChemAxon software (http://www.chemaxon.com/).

5.3.2 Filtration

The laboratory, dead-end membrane filtration cell used in this study was purchased for Membrane Extraction Technology Ltd, London, UK. The cell holds a maximum working volume of 270 ml. Membrane coupons fitted to the cell were round discs with effective diameter of 82 mm. During operation, pressure was provided to the cell by a nitrogen gas cylinder at constant value of 80 psi. A magnetic stirrer in the cell provided good mixing of the solution and reduces the concentration polarization effect. The speed was set at 600 rpm during filtration. Both feed and permeate solution samples were collected to vials at scheduled time and the weights were measured using electrical balance. Permeate and feed samples were not recycled back to the feed reservoir. All the parts in contact with solution are made of stainless steel or Teflon to minimize adsorption of the solutes. The system is depicted schematically in **Figure 5-2**.

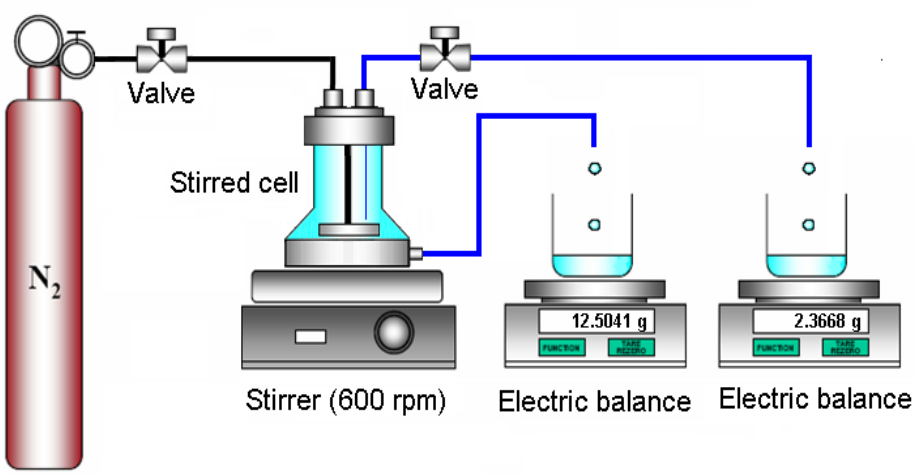


Figure 5-2. Schematic illustration of filtration experimental setup.

5.3.3 Adsorption

Static bench scale adsorption was conducted to test pH effect on adsorption. Prior to the experiment, the membrane was treated and cleaned with the same method as stated in filtration protocol. Organic solutions were also made using the same method as filtration experiments. In the experiments, 20 cm^2 membranes were cut into small pieces, and put into 40 ml vials together with 20 ml organic solutions, then the vials were shaken in a water bath to increase the mass transfer process. The solution concentration was monitored with time, until equilibrium was reached. The amount of organic adsorption by the membrane was calculated using mass balance. To be consistent with the filtration experiment, temperature in the shaker was set at 22 ±0.5 °C.

5.3.4 Numerical methods for non-linear PDE

In this study, a Matlab program was used to solve the transport equations. The core of the program is the command pdepe, which is essentially a Galerkin finite element method. The method is based on the algorithms developed by Skeel and Berzins (1990). Input parameters are listed in Table 5-4.

Table 5-4. Properties and model input parameters of solutes

Parameter	Phenol	2,4-DNP
Infinite diffusivity, D_∞ (cm^2/s)	9.0209×10^{-6}	6.9317×10^{-6}
Solute radius, r_p (nm)	0.238	0.309

5.4. Results and discussion

5.4.1 Adsorption uptake

In the batch sorption experiments, the empirical Freundlich isotherm model was employed to describe the sorption process. The experiments were conducted at four different pH values for phenol (4.0, 6.1, 8.0 and 10.0) and five pH values (3.0, 4.3, 6.0, 8.0 and 10.0) for 2,4-DNP. The percentage of protonated and unprotonated solutes at these pHs are shown in Table 5-5. The experimental data are plotted in Figures 5-3 and 5-4, and the Freundlich model parameters based on linear regression are presented in Tables 5-6 and 5-7.

Table 5-5. Solute Speciation

	pH	$[HA]/C_{T,A}$	$[A^-]/C_{T,A}$
phenol	4.0	1.0000	0.0000
	6.1	0.9999	0.0001
	8.0	0.9901	0.0099
	10.0	0.5000	0.5000
2,4-DNP	3.0	0.9407	0.0593
	4.3	0.4427	0.5573
	6.0	0.0156	0.9844
	8.0	0.0002	0.9998
	10.0	0.0000	1.0000

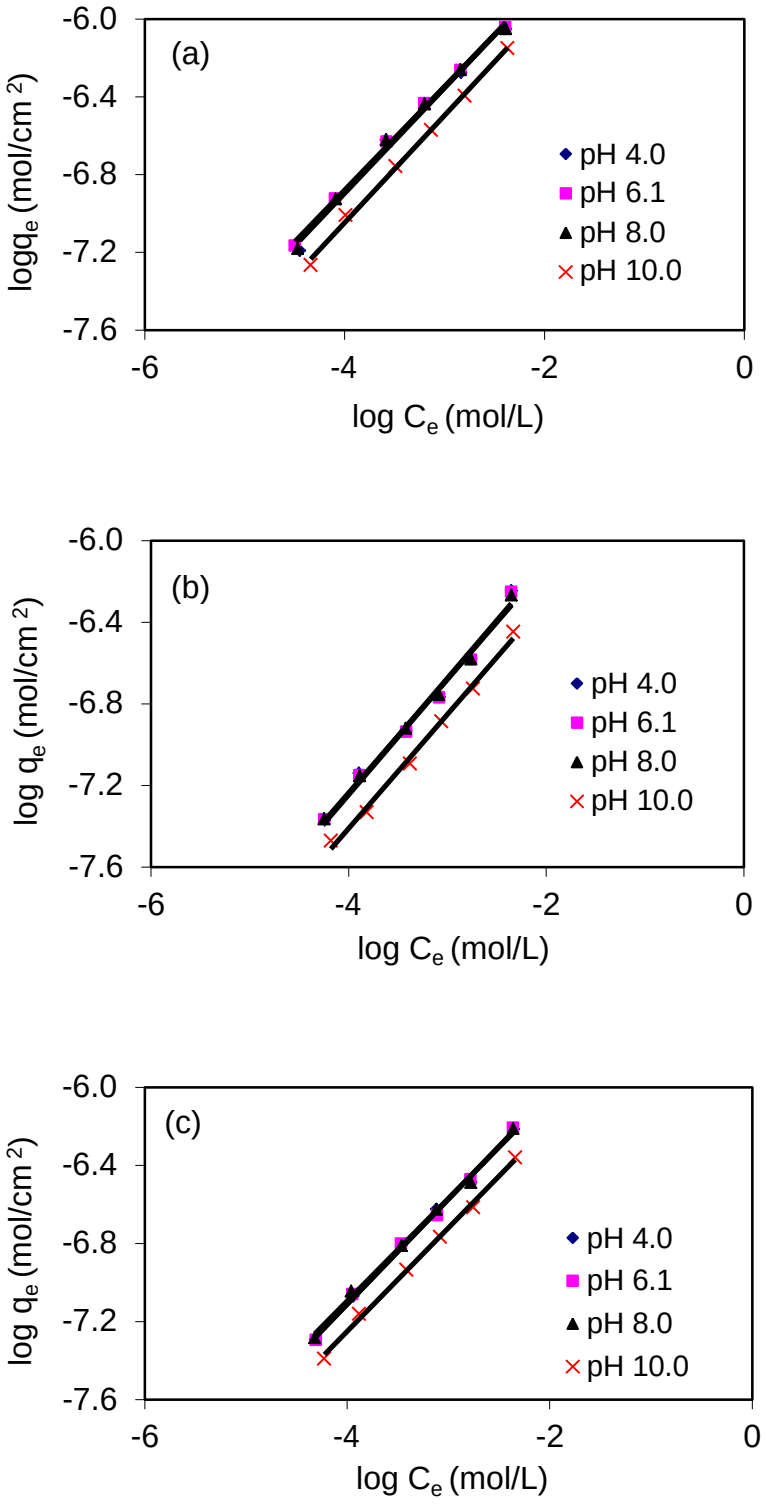


Figure 5-3. **pH effect on phenol adsorption isotherms of (a) NTR 7450 membrane; (b) NF 90 membrane; (c) NF 270 membrane. The Freundlich isotherm parameters are listed in Table 5.**

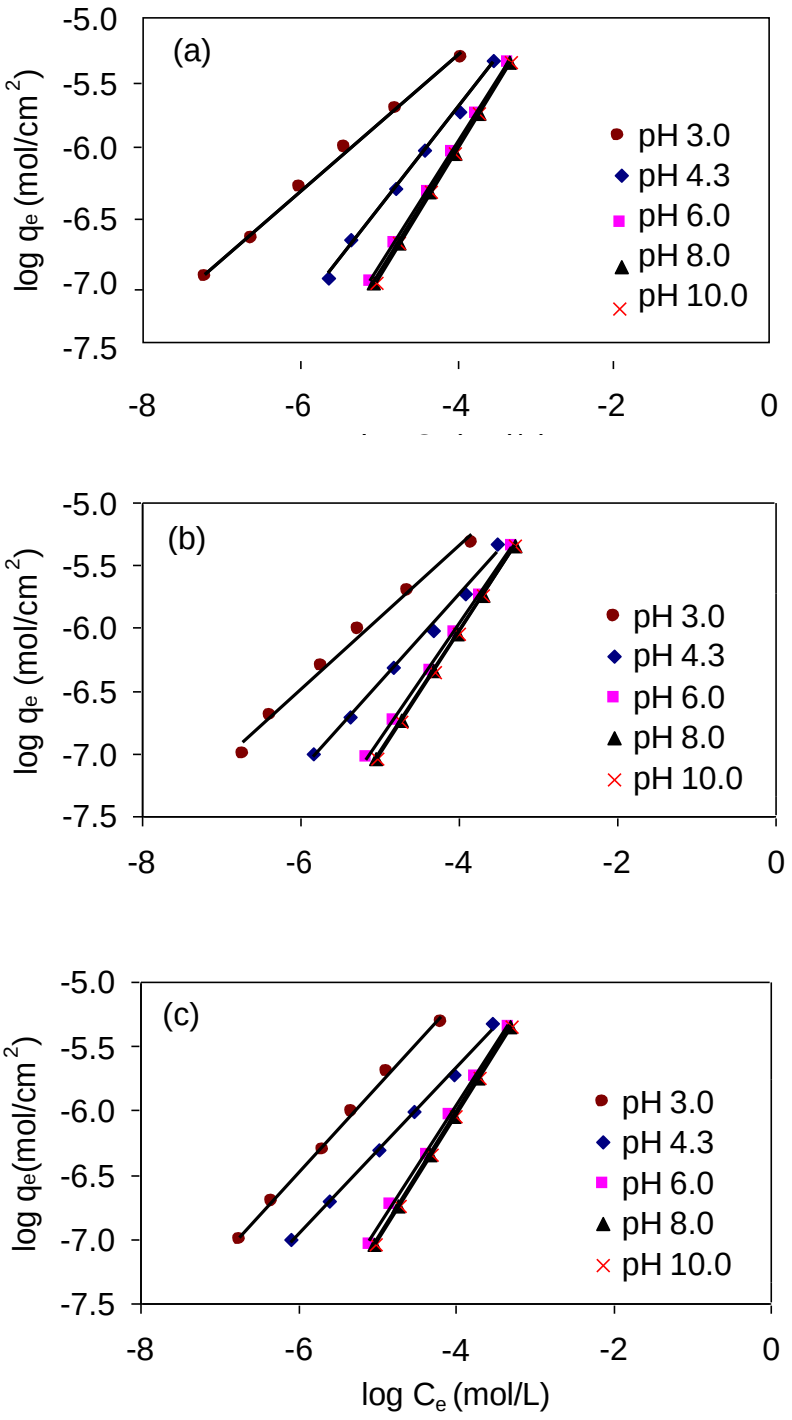


Figure 5-4. **pH effect on 2,4-dinitrophenol adsorption isotherms of (a) NTR 7450 membrane; (b) NF 90 membrane; (c) NF 270 membrane. The Freundlich isotherm parameters are listed in Table 6.**

Table 5-6. Freundlich Isotherm Parameters for Phenol Adsorption Isotherms

	pH	K_F	n	R^2
NTR 7450 membrane				
	4.0	1.87E-05	0.5424	0.9922
	6.1	1.78E-05	0.5325	0.9979
	8.0	1.86E-05	0.5397	0.9946
	10.0	1.44E-05	0.5518	0.9972
NF 90 membrane				
	4.0	1.06E-05	0.5665	0.9878
	6.1	1.03E-05	0.5645	0.9887
	8.0	9.93E-06	0.5581	0.9936
	10.0	6.68E-06	0.5589	0.9938
NF 270 membrane				
	4.0	1.10E-05	0.5379	0.9973
	6.1	1.11E-05	0.5397	0.9967
	8.0	1.02E-05	0.5263	0.9959
	10.0	7.39E-06	0.5296	0.9973

Table 5-7. Freundlich isotherm parameters for 2,4-DNP adsorption isotherms

Membrane	pH	K_F	*n*	R^2
NTR 7450	3.0	3.46E-03	0.6709	0.9979
	4.3	8.02E-04	0.6439	0.9979
	6.0	7.10E-03	0.9555	0.9994
	8.0	7.86E-03	0.9801	0.9999
	10.0	7.66E-03	0.9818	1.0000
NF 90	3.0	6.05E-04	0.5219	0.9958
	4.3	2.47E-03	0.7777	0.9973
	6.0	7.08E-03	0.9580	0.9998
	8.0	7.38E-03	0.9729	0.9999
	10.0	8.16E-03	0.9876	0.9999
NF 270	3.0	9.21E-04	0.5768	0.9912
	4.3	1.20E-03	0.7039	0.9940
	6.0	5.08E-03	0.9201	0.9994
	8.0	6.91E-03	0.9671	1.0000
	10.0	7.56E-03	0.9802	1.0000

From both the isotherm figures and the tabulated sorption parameters, it was found that solute speciation had a significant effect on adsorption. In the phenol sorption experiments, almost all the phenol was present as the protonated form at pH 4, 6.1, and 8, and adsorption isotherms were similar. In contrast, at pH 10, half of the phenol was ionized in solution, and as a result, the amount of sorbed solute was much less. Similar results were observed for 2,4-DNP sorption experiments; sorption was greatest at pH 3.0, and least above pH 6.0.

Results also showed that 2,4-DNP was adsorbed to a greater extent by all three membranes than phenol was. The presence of two nitro groups in the 2,4-DNP molecule make the molecule larger and thus 2,4-DNP has a significantly lower solubility and higher $\log K_{ow}$ relative to phenol (see Table 5-3). In addition, the nitro groups are strongly electron withdrawing, leaving the ring deficient in electron density, making 2,4-DNP an electron acceptor. Therefore, specific donor-acceptor interactions may enhance uptake. Other research has also identified adsorption of organic compounds by filtration membranes. Nghiem et al. (2004) noticed that estrogenic hormone retention by more porous membranes decreases with decreasing adsorption and the subsequent retention is relatively low. They concluded that an important removal mechanism of hormones by loose NF membranes was adsorption.

5.4.2 Permeate breakthrough curve

The measured feed and permeate solution concentration as a function of operating time for phenol and 2,4-DNP filtration experiments are shown as the symbols in **Figures 5-5 and 5-6**, respectively. In all the filtration experiments the concentration of feed solution was kept approximately constant during the entire filtration process, while permeate concentration increased rapidly. Also note that the shape of the permeate concentration profile is similar to breakthrough curves typical of short activated carbon fixed beds.

Solute retention (rejection) was calculated from the feed and permeate concentrations using $R = 1 - C_p/C_f$. The results in Figures 5-5 and 5-6 show that NTR 7450 had a higher retention for both phenol and 2,4-DNP as compared to the NF 90 and NF 270 membranes. As tabulated in Table 1, the pore radius of NTR 7450 membrane is almost bigger than that of NF 90 and NF 270 membranes, thus the higher solute retention of NTR 7450 membrane could not be due to the size exclusion. Solute adsorption is a likely explanation for the higher retention of the NTR 7450 membrane compared to NF 90 and NF 270 membranes, consistent with the static adsorption experiment results.

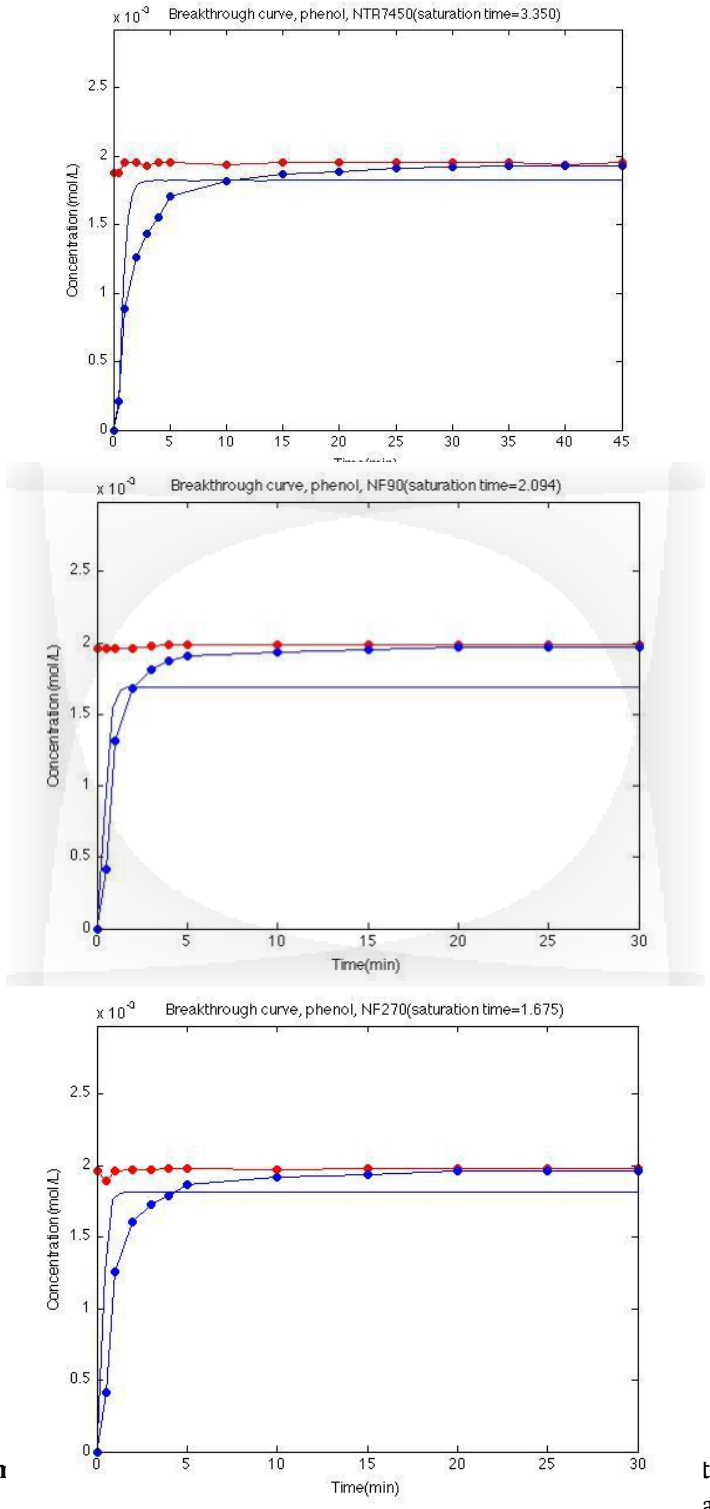


Figure 5-5. Pern tration time for (a) NTR 7450 membrane, (b) NF 90 membrane, (c) NF 270 membrane.

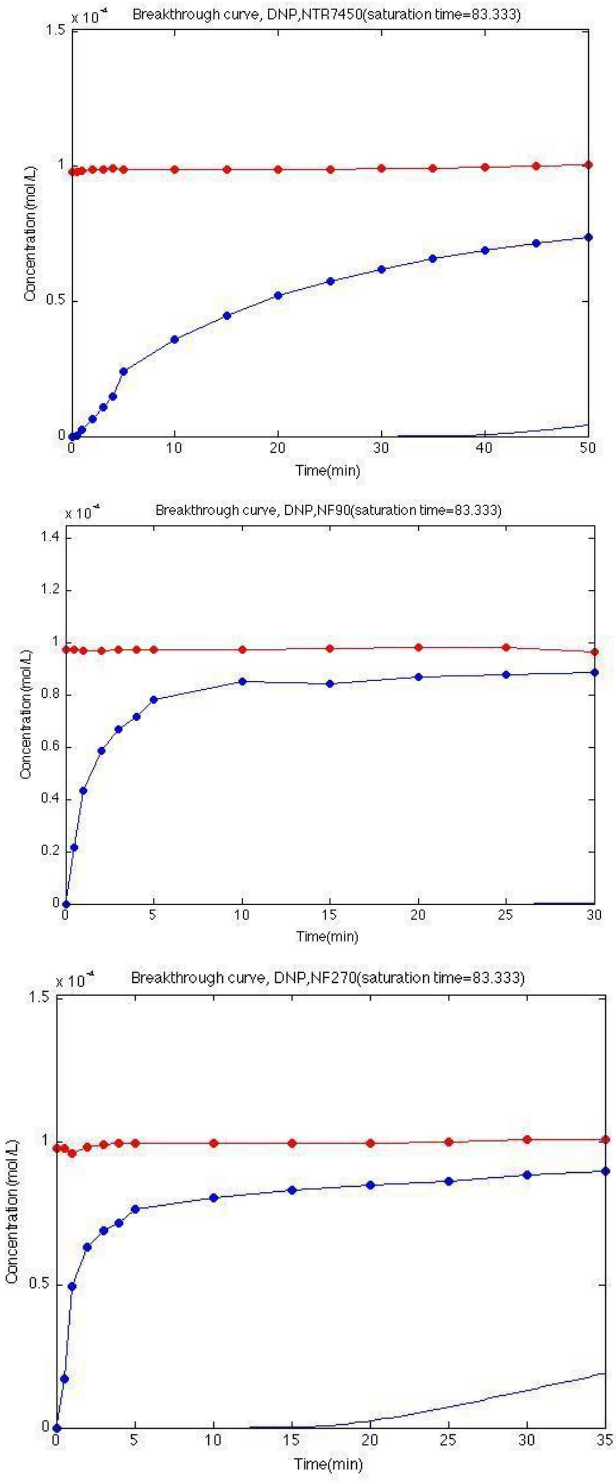


Figure 5-6. Perr ltration time for (a) NTR ne.

5.4.3 Modeling

The dynamic model can provide concentration profiles over both time and distance. As shown by the solid lines in **Figures 5-5 and 5-6**, the model has a relatively good result on the filtration of phenol, with a slight overestimation of rejection and underestimation of the time to reach steady state (retention time). The reason for the overestimation of rejection for neutral molecules was studied by Verliefde et al. (2009). It is believed that the affinity of the compounds to the membrane will contribute to the partition coefficient, which will lead to larger concentration inside the pores and then it can further lead to a lower rejection and a larger adsorption amount. It is also possible that the dispersion of the solutes in the support layer will also contribute to the retention time, given the fact that the support layer itself is also porous polymer and much thicker than the active layer.

As for the 2,4-DNP, it seems to have a larger overestimation on rejection and even larger over estimation on retention time. The reason for the larger overestimation on rejection could be result in a higher affinity to the membrane, which is consistent with its high adsorption uptake, even though the membranes are also negatively charged. And as for retention time, it seems like during the actually filtration, the adsorption is not as significant as in the batch experiments. It could be explained by the equilibrium time—even though the 2,4-DNP has a larger adsorption tendency, the electrostatic repulsion result in a much longer time for the adsorption meets equilibrium, and as a result during the filtration, only part of the adsorption capacity was actually used. It is also interesting that the overestimation of rejection seems to be in consistent with the adsorption parameter K_F. It indicates that the adsorption capacity could be used to estimate the affinity of the solutes to membrane during filtration experiments.

5.4.4 Flux decline

Solutes adsorbed by membrane will be attached on the membrane surface or inside of pores. Those molecules inside the pores will narrow the free pathway of the water flow. When the adsorption effect is strong, it could even lead to pore blocking, especially when the solute and membrane pore sizes are similar (λ approaches to 1). All these effects reduce the membrane permeability and lead to flux decline.

Figure 5-7 shows the permeate flux of phenol and 2,4-DNP solutions filtration by all three NF membranes during the entire filtration process. Results show that except phenol filtration with NF 90 membrane, all other experiments exhibited flux decline, with the largest value around 7%. Comparing this figure with the results of static adsorption experiments, we could see that the flux decline was bigger when the solute uptake capacity by membranes was higher. This result is consistent with Van der Bruggen's finding. He discussed various the flux decline mechanisms during nanofiltration of organic compound in aqueous solution, and found that adsorption resulted in a strong decrease of water flux for uncharged organic compounds filtration.

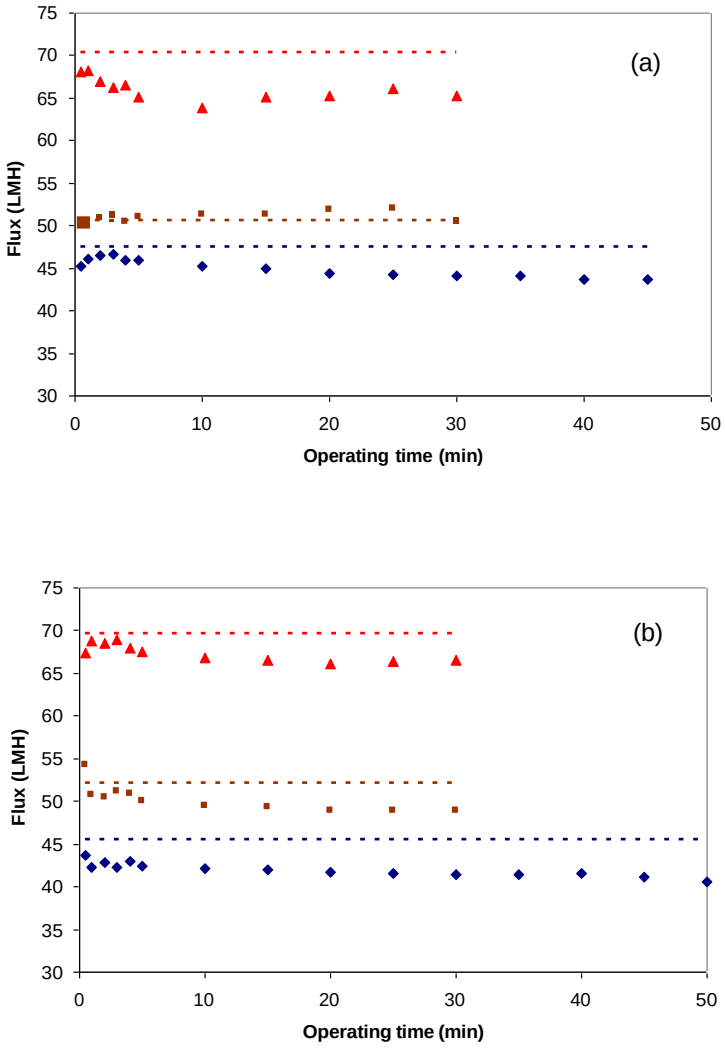


Figure 5-7. Flux decline during (a) 0.002 mol/l phenol and (b) 0.0001mol/l 2,4-DNP solutions filtration. Dashed lines represent DI water flux of three membranes before filtration. Symbols represent flux of permeate solution through (◆) NTR 7450 membrane, (■) NF 90 membrane, and (▲) NF 270 membrane.

5.5. Conclusions and Future Work

The following conclusions can be reached as a result of this work:

1. Low pH can promote the adsorption of phenolic compounds by membranes. 2,4-DNP exhibits larger adsorption uptake than phenol. Hydrophobic forces and perhaps donor-acceptor interactions overcome potential electrostatic repulsion.

2. 2,4-DNP has a much higher rejection than phenol, likely a combination of larger molecular size and greater electrostatic repulsion.

3. The dynamic model developed can predict the breakthrough behavior of phenol on three membranes, with a slight overestimation of rejection and underestimation of the retention time, which may be explained by the affinity of the molecules to membrane.

4. 2,4-DNP (negatively charged) shows a much smaller adsorption tendency in filtration experiments. A possible explanation is the difficulty of the compounds approaching the membrane surface with the same charge, hence, a longer equilibrium time.

5. For both phenol and 2,4-DNP, the overestimation of rejection, which could be explained by the underestimation of partition coefficient, is in agreement with the adsorption parameter K_F. The adsorption tendency could be used as an indicator for the affinity of the molecules to the membranes.

6. Flux decline (with the largest value around 7%) is observed, consistent with the adsorption experiments.

7. This study provides valuable insights into future experiments on the removal of chemical additives.

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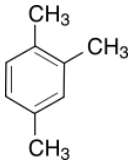
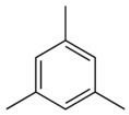
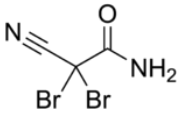
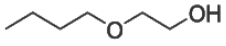
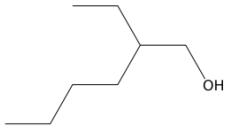
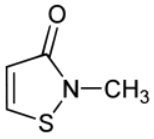
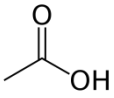
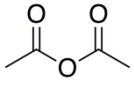
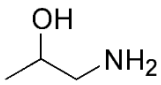
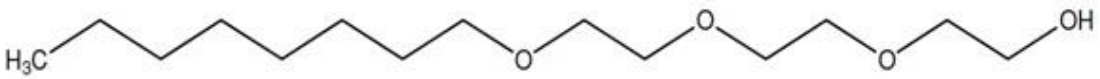
APPENDIX 1

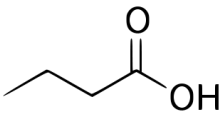
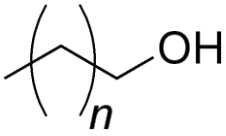
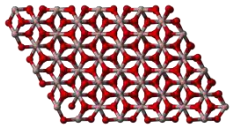
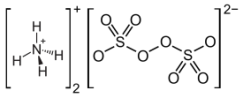
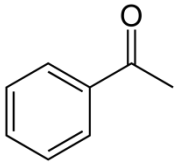
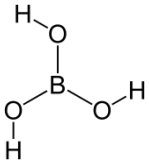
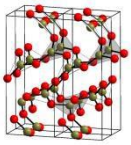
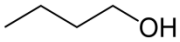
Selected Chemicals Used by Hydraulic Fracturing Companies in Pennsylvania For Surface and Hydraulic Fracturing Activities

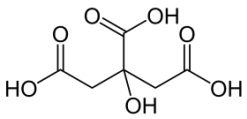
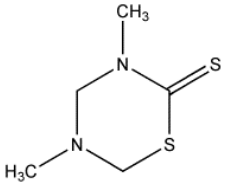
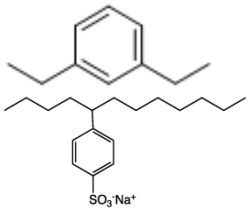
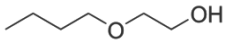
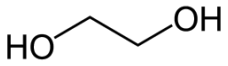
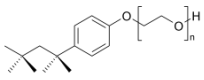
List prepared by the Department of Environmental Protection, Bureau of Oil and Gas Management.
Source: Material Safety Data Sheets obtained from Industry

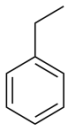
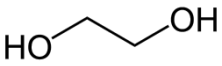
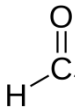
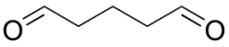
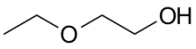
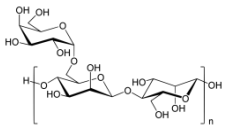
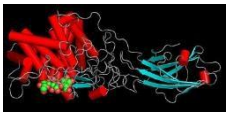
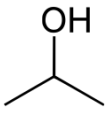
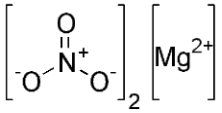
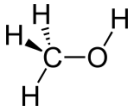
Compound	Notes	Structure
1,2,4-Trimethylbenzene	Aromatic hydrocarbon; occurs naturally in petroleum (about 3%); used as a liquid scintillator, sterilizing agent, gasoline additive.	
1,3,5 Trimethylbenzene	Aromatic hydrocarbon	
2,2-Dibromo-3-Nitrilopropionamide	biocide used to control algae, bacteria, fungi and yeasts. Unstable in water; degrades to ammonia and bromine ions.	
2-butoxyethanol	butyl ether of ethylene glycol. Nonvolatile, inexpensive solvent, degreaser, with modest surfactant properties.	
2-Ethylhexanol	low volatility solvent	
2-methyl-4-isothiazolin-3-one	powerful biocide and preservative within the group of isothiazolinones, used in shampoos and body care products	
5-chloro-2-methyl-4-isothiazolin-3-one	Biocide; mixture with above sold as Kathon; replaced tributyltin as the antifouling agent of choice in ship hull paint.	As above with chlorine substituent
Acetic Acid	Anti-scalant, component of vinegar	
Acetic Anhydride		

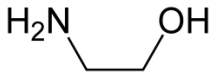
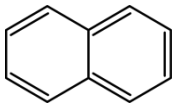
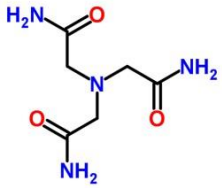
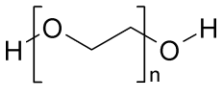
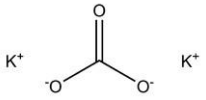
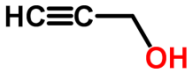
Acid Pensurf	(2-ethylhexanol (40 to 70%) + dodecylbenzenesulfonate isopropanolamine 30 to 60%); surfactant, cleaner	 isopropanolamine
Alcohol Ethoxylated	See: ethoxylated alcohol	

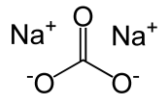
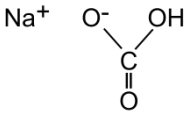
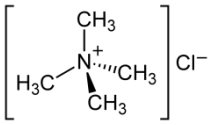
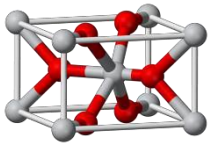
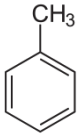
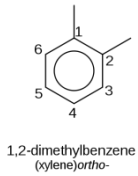


Aliphatic Acid	General class of organic compounds containing an acid group and an alkyl chain, $C_nH_{2n+1}COOH$	
Aliphatic Alcohol	A series of organic compounds of the structure $C_nH_{2n+1}OH$, methanol and ethanol are the first members	
Aluminum Oxide	Corundum, Al_2O_3. Abrasive	
Ammonium Bifluoride	Etchant	NH_4HF_2 or $NH_4F{\cdot}HF$
Ammonia Bisulfite	Reductant, oxygen scavenger, bleaching agent, sterilizing agent	NH_4HSO_3
Ammonia Persulfate	oxidant	
Ammonium chloride	Controls clay swelling	NH_4Cl
Ammonium Salt	Class of compounds containing NH_4	
Aromatic Hydrocarbon	See: benzene derivatives	
Aromatic Ketones	Class of compounds of which acetophenone is the simplest	
Boric Acid	A weak acid of boron often used as an antiseptic or insecticide	
Boric Oxide	Oxide of boron, e.g., B_2O_3	
Butan-1-0l (n-butanol)	Aliphatic alcohol, solvent	

Citric Acid	Metal chelating agent	
Crystalline Silica: Cristobalite		
Crystalline Silica: Quartz		
Dazomet	3,5-Dimethyltetrahydro-1,3,5-thiadiazine-2-thione. Antimicrobial agent with algaecidal, bacteriocidal, fungicidal, microbicidal, and mildewcidal properties.	
Diatomaceus Earth	naturally occurring, soft, siliceous sedimentary rock consists of fossilized remains of diatoms, a type of hard-shelled algae; filter media, absorbent, abrasive	
Diesel (use discontinued)	Lubrication, enhanced shale inhibition, and cleaning ability, low viscosity	
Diethylbenzene	solvent	
Doclecylbenzene Sulfonic Acid	surfactant	
Butyl Cellosolve (2-BE)	2-Butoxyethanol is a water miscible glycol ether solvent - used in latex paint; see glycol ethers	
Ethane-1,2-diol	Ethylene glycol; corrosion, hydrate control, scale inhibitor	
Ethoxlated Alcohol	Class of non-ionic surfactants produced from an alcohol and ethylene oxide: ROH + nC_2H_4O → $R(OC_2H_4)_nOH$ to produce an anionic surfactant. R generally a C8 to C18 chain. Used in laundry detergents and other cleaners.	
Ethoxylated Octylphenol	As above; ROH replaced by octylphenol. Surfactant, DOW Triton X family; Triton X-100 (n = 10) shown; n varies	

Ethylbenzene	solvent	
Ethylene Glycol	See: Ethane-1,2-diol	
Ethylhexanol	See: 2- Ethylhexanol	
Ferrous Sulfate Heptahydrate	Reductant, flocculant	$FeSO_4 \cdot 7H_2O$
Formaldehyde	Simplest aldehyde; disinfectant, biocide	
Glutaraldehyde	Disinfectant, algaecide	
Glycol Ethers (includes 2BE)	group of solvents based on alkyl ethers of ethylene glycol, $CH_3(CH_2)_nOCH_2CH_2OH$; e.g., n = 1 yields 2-Ethoxyethanol, also known by the trademark Cellosolve or ethyl cellosolve	
Guar gum	Polysaccharide, viscosity control	
Hemicellulase enzyme	Hydrolyzes cellulose; widely used in textile industry and in laundry detergents.	
Hydrochloric acid	Strong acid	HCl
Hydrotreated light distillate	Mineral turpentine, refined C6 to C9 hydrocarbon distillate; solvent	
Iron Oxide	used in aqueous solutions for scrubbing certain acidic gases	
Isopropyl Alcohol, isopropanol	Solvent	
Kerosene	lubricant; micron sized oil particles, composition varies	
Magnesium Nitrate		
Mesh Sand (Crystalline Silica)	propant	
Methanol	Solvent, corrosion inhibitor	

Monoethanolamine	Used for alkalinization of water	
Naphthalene	Sulfonated form used as a nondetergent wetting agent, colloidal dispersant	
Nitrilotriacetamide	Anti-scalant, chelating agent	
Oil Mist	Lubricant, formula and structure varies	
Petroleum distillate blend	See: petroleum distillates	
Petroleum distillates	Class of substances, light distillates (LPG, gasoline, naphtha), middle distillates (kerosene, diesel)	
Petroleum naphtha	Range of different refinery intermediate products; complex mixture of hydrocarbon molecules generally having between 5 and 12 carbon atoms.	
Polyethoxylated Alkanol (1)	See: Ethoxylated alcohol	
Polyethoxylated Alkanol (2)	See: Ethoxylated alcohol	
Polyethylene Glycol Mixture	Polymer of ethylene oxide; lubricant, dispersant	
Polysaccharide	See Guar Gum	
Potassium Carbonate	pH adjustment	
Potassium Chloride	used in water as a completion fluid in petroleum and natural gas operations	KCl
Potassium Hydroxide	Strong base	KOH
Prop-2-yn-1-0l, Propargyl Alcohol	corrosion inhibitor, a metal complex solution, a solvent stabilizer	
Propan-2-0l	See: isopropyl alcohol	

Sodium Ash	Soda ash, Na_2CO_3, pH adjustment	
Sodium Bicarbonate	$NaHCO_3$, pH adjustment	
Sodium Chloride	NaCl, salt	
Sodium Hydroxide	NaOH, strong base, pH adjustment	
Sucrose	sugar	
Tetramethylammonium Chloride		
Titanium Oxide	TiO2, rutile. Propant?	
Toluene	Methyl benzene, solvent	
Xylene	di-methyl benzene, solvent (three isomers)	 1,2-dimethylbenzene (xylene)*ortho-*

Hydraulic Fracturing and the Management, Disposal, and Reuse of Frac Flowback Waters: Views from the Public in the Marcellus Shale

ABSTRACT

Issues associated with the public's views on hydraulic fracturing and the management, disposal, and reuse of frac flowback wastewaters are empirically examined in this paper. The data used in the analyses were collected in a general population survey from a random sample drawn from 21 counties located in the geological Central Core and Tier 1 of the Marcellus Shale region in Pennsylvania. Differences in the information reported by survey respondents living in high well-density counties (20 or more wells per 100 square miles) and their counterparts living in low well-density counties (fewer than 20 wells per 100 square miles) were examined. Substantive findings from the overall sample, as well as statistically significant differences between the two groups of respondents, are reported. The results contained in this paper should prove beneficial to members of the general public, community leaders, oil and gas industry representatives, government and regulatory agency personnel, environmental and non-governmental organization representatives, and other interested stakeholders.

1. Introduction

Technological advances in horizontal drilling and multi-stage hydraulic fracturing were two primary factors that contributed to the unprecedented shale gas boom during the past decade in the United States [1, 2]. Horizontal drilling techniques and hydraulic fracturing methods developed, tested, and refined in the Barnett Shale during the late 1990s and early 2000s were rapidly employed in shale gas basins across the nation (e.g., Fayetteville, Woodford, Haynesville, Marcellus, Utica, Eagle Ford). According to the Energy Information Administration (EIA), the statistical and analytical agency of the U.S. Department of Energy, shale gas contributed roughly one third of the total U.S. natural gas production (7.8 tcf of 23.0 tcf) as of 2011 [3]. Further, EIA estimates shale gas production will constitute approximately one half (50.5 percent; 16.7 tcf) of the projected 33.1 tcf total domestic natural gas production in 2040 [3].

A barrage of controversy accompanied this tremendous surge in shale gas production [4, 5]. At the center of the debate is the well stimulation/completion process known as hydraulic fracturing [6, 7, 8, 9]. Shale gas development relies heavily on multi-stage hydraulic fracturing stimulation to maximize commercial viability. Wells are hydraulically fractured by flushing large quantities of "frac fluid" – a mixture of freshwater, proppants, and small amounts of friction reducers and other chemicals – into them at extremely high pressure levels to create small cracks, or "fractures," in the shale formations. Doing this allows natural gas to flow more freely through the reservoir and, in turn, increases recovery. Frac jobs commonly use 1 to 3 million gallons of water per gas well; in some cases, water use may exceed 5 million gallons per frac [10].

After a frac job is completed, the pressure is released and, along with the natural gas, the well generates frac flowback and produced waters. Frac flowback is the term used to describe

injected water that returns to the surface during the first few weeks of production. Produced water refers to the water naturally present in the formation brought to the surface throughout the production process [2]. Both frac flowback and produced waters generally contain high levels of total dissolved solids (TDS) and other contaminants. Operators must manage and dispose of flowback and produced waters using methods in compliance with state and local regulatory requirements.

Until recently, energy producers used several methods to manage and dispose of flowback and produced wastewaters from shale reservoirs, including underground injection, surface discharge, municipal wastewater treatment plant discharge, commercial industrial wastewater treatment discharge, and beneficial reuse [2]. Underground injection is the primary wastewater management/disposal method employed in the vast majority of shale gas basins [2]. Beneficial reuse remains the management/disposal method least adopted and diffused throughout the industry [11]. However, in efforts to conserve freshwater resources, reduce social and environmental impacts, improve public confidence, and minimize costs, operators have recently begun to treat and reuse flowback and produced waters in subsequent drilling and hydraulic fracturing operations [2, 12].

The purpose of this paper is to empirically explore issues associated with hydraulic fracturing and the management and disposal of frac flowback wastewater. Here, survey data gathered in Pennsylvania's Marcellus Shale region were analyzed to investigate respondents' levels of familiarity with: (1) the process of hydraulic fracturing; (2) the management and disposal of frac flowback wastewater; and, (3) frac flowback wastewater treatment technology. Further, we examine the contribution made to self-reported knowledge of hydraulic fracturing by eight different sources and the amount of trust in each of the same sources to deliver unbiased,

factual knowledge about the topic. Building upon previous research on the public's perception of produced water by Theodori and his colleagues [13, 14], we assess the level of agreement that treated wastewater from hydraulic fracturing operations could safely be used for selected purposes. Finally, we evaluate the association between level of familiarity with frac flowback wastewater treatment technology and the proposed potential uses of treated wastewater. Differences in information reported by respondents living in high well-density counties (20 or more wells per 100 square miles) and their counterparts living in low well-density counties (fewer than 20 wells per 100 square miles) are examined.

2. Data Collection

Between June and October 2012, a random sample of individuals living in 21 counties located in the geological Central Core and Tier 1 of the Marcellus Shale region in Pennsylvania were contacted by telephone or mail and asked to participate in a survey of resident opinions concerning natural gas development.[1] All counties included in the sampling frame had experienced at least some Marcellus Shale drilling, but the density of such wells varied widely. To secure opinions from respondents within this region that reflected gas-industry activity differences, the sample was chosen to reflect the views of individuals living in counties with "low" well densities (fewer than 20 wells per 100 square miles) and those living in counties with "high" well densities (20 or more wells per 100 square miles). Coincidentally, 50% of the total population in the 21 counties included in the sample fell in the low well-density counties and 50% fell in the high well-density counties.[2]

The telephone survey was conducted over the period June 11, 2012, to August 30, 2012, using state-of-the-art CATI software designed to maximize completed surveys from the limited

and finite random sample pool over an extended period of time. This meant repeated calls to each unique number at various times of the day and days of week and repeated callbacks to those individuals who expressed interest in participating, when reaching them due to busy schedules was a challenge. Calls continued until 200 completed interviews were obtained from each of the well-density county categories. The overall telephone survey completion rate was 27%.[3]

For the mail survey, 800 names and addresses of persons with listed telephone numbers were randomly selected from the low well-density counties, and 800 names and addresses were randomly selected from the high well-density counties. An initial mailing, including a cover letter and a printed questionnaire, was sent to these sample members in July 2012, followed by three follow-up reminder letters with duplicate questionnaires over the next three months. A total of 43 questionnaires in the low well-density counties and 52 questionnaires in the high well-density counties were returned as undeliverable. Since one objective of the larger study was to examine the differential effects of results from telephone and mail surveys [16,17], the same protocol used in the conduct of the telephone survey was used in the mail survey. Hence, only the first 200 replies received from each of the well-density categories were included in the current analysis, resulting in an overall usable response rate of 27%.[4]

3. Measurement of Variables

The questions/items used in the mail and telephone surveys were identical in wording and in the instructions given to the respondents. The ways in which the specific questions/items used in this analysis were measured are specified below.

3.1. Measuring Familiarity with the Process of Hydraulic Fracturing

Familiarity with the process of hydraulic fracturing was assessed using a single survey item that ranged from 1 (extremely unfamiliar) to 7 (extremely familiar).

3.2. Measuring Contribution Made to Knowledge about the Process of Hydraulic Fracturing

Respondents were asked to indicate the degree to which each of eight sources contributed to what they knew about the process of hydraulic fracturing. The eight sources included: (1) newspapers; (2) *Gasland* (the film by Josh Fox); (3) natural gas industry; (4) regulatory agencies; (5) conservation/environmental groups; (6) Cooperative Extension; (7) university professors; and, (8) landowner groups/coalitions. Response categories were coded: 0 = none; 1 = very little; 2 = some; and, 3 = a great deal.

3.3. Measuring Trust to Deliver Unbiased, Factual Knowledge on Hydraulic Fracturing

Respondents were asked to indicate the amount of trust in each of the same eight sources to deliver unbiased, factual knowledge on the process of hydraulic fracturing. The sources were: (1) newspapers; (2) *Gasland*; (3) natural gas industry; (4) regulatory agencies; (5) conservation/environmental groups; (6) Cooperative Extension; (7) university professors; and, (8) landowner groups/coalitions. Response categories were coded as follows: 0 = no trust; 1 = very little trust; 2 = some trust; and, 3 = great deal of trust.

3.4. Measuring Familiarity with the Management and Disposal of Frac Flowback Water in the Marcellus Shale

Familiarity with the management and disposal of frac flowback water in the Marcellus Shale was assessed using a single survey item that ranged from 1 (extremely unfamiliar) to 7 (extremely familiar).

3.5. Measuring Familiarity with Frac Flowback Wastewater Treatment Technology

Familiarity with frac flowback wastewater treatment technology was assessed using a single survey item that ranged from 1 (extremely unfamiliar) to 7 (extremely familiar).

3.6. Measuring Potential Uses of Treated Wastewater from Hydraulic Fracturing Operations

Potential uses of treated wastewater from hydraulic fracturing operations were evaluated with a list of six practices. Respondents were asked whether they believed that treated wastewater from hydraulic fracturing operations could be safely used for: (1) re-use by gas and oil industry operators; (2) watering of livestock; (3) industrial use (e.g., manufacturing, etc.); (4) people's drinking water; (5) municipal uses (e.g., watering of golf courses and city parks, etc.); and, (6) irrigation of farmland.

3.7. Mode of Data Collection

Previous analyses of data from the larger study found differences between responses to the telephone and mail surveys [16, 17]. As a result, mode of data collection (0 = telephone survey; 1 = mail survey) was incorporated as a control variable in each analysis below.

4. Findings

4.1. Familiarity with the Process of Hydraulic Fracturing

4.1.1. Overall Results

In total, one of every five respondents (20%) reported being *extremely unfamiliar* with the process of hydraulic fracturing, and an additional 23 percent rated their familiarity at "2" or "3" on the seven point scale. Conversely, approximately 9 percent of respondents indicated they were *extremely familiar* with the hydraulic fracturing process and about three of ten (31%) indicated they had some familiarity (scores 5 and 6 on the scale). The mean level of familiarity with the process of hydraulic fracturing was 3.73 (SD = 1.91).

4.1.2. Results for Respondents in Low Well-density Counties versus High Well-density Counties

Roughly one in four respondents (23.7%) living in the low well-density counties reported being *extremely unfamiliar* with the process of hydraulic fracturing, compared to 16.3 percent of respondents living in the high well-density counties. In the low well-density counties, 7.6 percent of respondents reported being *extremely familiar* with the process of hydraulic fracturing, compared to 9.8 percent in the high well-density counties. An analysis of covariance revealed that, adjusting for differences between mode of data collection, the mean level of familiarity with the process of hydraulic fracturing for respondents in the high well-density counties ($M = 3.90$, $SD = 1.89$) was significantly higher ($p \leq 0.05$) than for respondents in the low well-density counties ($M = 3.55$, $SD = 1.92$).

4.2. Contribution Made to Knowledge about the Process of Hydraulic Fracturing

4.2.1. Overall Results

The eight sources that may or may not have contributed to what respondents knew about hydraulic fracturing were ranked in ascending order by overall mean score (see Table 1). Newspapers ($M = 1.71$) were the sources of information that contributed most to respondents' knowledge of the hydraulic fracturing process, followed by the natural gas industry ($M = 1.30$) and conservation/environmental groups ($M = 1.21$). *Gasland* ($M = 0.41$) was the source of information that contributed least to respondents' knowledge of hydraulic fracturing.

4.2.2. Results for Respondents in Low Well-density Counties versus High Well-density Counties

The pattern of results for each subgroup of respondents mirrored the overall sample. Newspapers were the sources of information that contributed most to respondents' knowledge of the hydraulic fracturing process in both the low well-density counties ($M = 1.73$) and high well-density counties ($M = 1.69$); *Gasland* was the source of information that contributed least to

respondents' knowledge of hydraulic fracturing in both county types (M = 0.39 in low well-density counties and M = 0.43 in high well-density counties).

The statistical significance of the observed differences between the respondents from low well-density counties and high well-density counties regarding sources of information that may or may not have contributed to their knowledge of hydraulic fracturing were tested using analysis of covariance tests. Results revealed that respondents living in high well-density counties were significantly more likely than those living in low well-density counties to report that the natural gas industry ($p \leq 0.01$) and regulatory agencies ($p \leq 0.05$) contributed to their knowledge of hydraulic fracturing, controlling for the differences in mode of data collection.

[insert Table 1 about here]

4.3. Trust to Deliver Unbiased, Factual Knowledge on Hydraulic Fracturing

4.3.1. Overall Results

The eight sources respondents may or may not trust to deliver unbiased, factual knowledge on hydraulic fracturing were ranked in ascending order by overall mean score (see Table 2). University professors and conservation/environmental groups tied as the sources respondents trusted most to deliver unbiased, factual knowledge on the hydraulic fracturing process (M = 1.57). These two sources were followed closely by newspapers (M = 1.56) and landowner groups/coalitions (M = 1.53). *Gasland* (M = 0.80) was the respondents' least-trusted source of information.

4.3.2. Results for Respondents in Low Well-density Counties versus High Well-density Counties

Respondents in the low well-density counties rated university professors (M = 1.61) as the source they trusted most to deliver unbiased, factual knowledge on hydraulic fracturing, followed by conservation/environmental groups (M = 1.59) and newspapers (M = 1.58). In the

high well-density counties, respondents rated conservation/environmental groups (M = 1.55) and newspapers (M = 1.55), followed by university professors (M = 1.53) and landowner groups/coalitions (M = 1.53) as their most trusted sources. *Gasland* was the source of information respondents trusted the least (M = 0.81 in low well-density counties and M = 0.79 in high well-density counties).

The statistical significance of the observed differences between the respondents from low well-density counties and high well-density counties with respect to sources of information they may or may not trust to deliver unbiased, factual knowledge on hydraulic fracturing was tested using analysis of covariance tests. Two of the eight sources were found to differ significantly – respondents living in high well-density counties were more likely than those living in low well-density counties to trust regulatory agencies ($p \leq 0.05$) and the natural gas industry ($p \leq 0.01$), adjusting for differences in mode of data collection.

[insert Table 2 about here]

4.4. Familiarity with the Management and Disposal of Frac Flowback Water in the Marcellus Shale

4.4.1. Overall Results

Approximately one third of the respondents (33.2%) reported being *extremely unfamiliar* with the management and disposal of frac flowback water in the Marcellus Shale. Conversely, 6.8 percent of respondents indicated they were *extremely familiar* with the management and disposal of frac flowback water in the region. The mean level of familiarity with the management and disposal of frac flowback water in the Marcellus Shale was 3.06 (SD = 1.94).

4.4.2. Results for Respondents in Low Well-density Counties versus High Well-density Counties

Among respondents living in low well-density counties, 36.9 percent reported being *extremely unfamiliar* with the management and disposal of frac flowback water in the Marcellus Shale; roughly three in ten respondents (29.6%) living in the high well-density counties indicated the same lack of familiarity. In the low well-density counties, 5.8 percent of respondents reported being *extremely familiar* with the management and disposal of frac flowback water in the Marcellus Shale, compared to 7.8 percent of respondents in the high well-density counties.

The mean level of familiarity with the management and disposal of frac flowback water in the Marcellus Shale was 2.94 (*SD* = 1.93) for respondents in the low well-density counties and 3.18 (*SD* = 1.94) for respondents in the high well-density counties. The difference between the two groups of respondents failed to attain statistical significance at the 0.05 level.

4.5. Familiarity with Frac Flowback Wastewater Treatment Technology

4.5.1. Overall Results

Almost four in ten respondents (38.5%) reported being *extremely unfamiliar* with frac flowback wastewater treatment technology. Conversely, 3.1 percent of respondents indicated they were extremely familiar with frac flowback wastewater treatment technology. The mean level of familiarity with frac flowback wastewater treatment technology was 2.69 (*SD* = 1.78).

4.5.2. Results for Respondents in Low Well-density Counties versus High Well-density Counties

Among respondents living in the low well-density counties, 42.6 percent reported being *extremely unfamiliar* with frac flowback wastewater treatment technology, compared to roughly one third of respondents (34.3%) living in the high well-density counties. In the low well-density counties, 2.5 percent of respondents reported being extremely familiar with frac flowback wastewater treatment technology, compared to 3.8 percent of respondents in the high well-density counties.

The mean level of familiarity with frac flowback wastewater treatment technology was 2.57 (*SD* = 1.75) for respondents in the low well-density counties and 2.82 (*SD* = 1.80) for respondents in the high well-density counties. Analysis of covariance revealed this difference was statistically significant ($p \leq 0.05$).

4.6. Potential Uses of Treated Wastewater from Hydraulic Fracturing Operations

The six potential uses of treated wastewater from hydraulic fracturing operations were ranked in ascending order by the percentage of respondents indicating "yes" (see Table 3). Approximately eight in ten respondents (81%) believed re-use in the gas and oil industry was the safest potential use. More than three in four respondents (77%) believed treated wastewater from hydraulic fracturing operations could safely be used for industrial use (e.g., manufacturing, etc.), whereas slightly more than one half of respondents (52%) agreed such water could be used for municipal purposes (e.g., watering of golf courses and city parks, etc.). Roughly three in ten respondents (31%) and two in ten respondents (19%), respectively, agreed irrigation of farmland and watering of livestock could safely be accomplished with the use of treated wastewater from hydraulic fracturing operations. Finally, 11 percent of respondents believed that treated wastewater from hydraulic fracturing operations could safely be used by humans as potable water.

Significance tests for the difference in the proportion of respondents from low well-density counties and those from high well-density counties who perceived safe potential uses of treated wastewater from hydraulic fracturing operations were examined using analysis of covariance. The results revealed respondents in high well-density counties were significantly more likely than their counterparts in low well-density counties to agree that treated wastewater from hydraulic fracturing operations could safely be re-used by gas and oil industry operators (*p*

$\leq$ 0.01), controlling for mode of data collection. For none of the other uses did the low- and high-density areas differ significantly in the perceptions of safe usages.

[insert Table 3 about here]

Following previous research on the public perception of desalinated produced water from oil and gas field operations [13, 14], we examined the associations between level of familiarity with frac flowback wastewater treatment technology and the perceived safe potential uses of treated wastewater from hydraulic fracturing operations using bivariate and multivariate logistic regression techniques. As in the produced water studies [13, 14], gender and level of education were included in the multivariate models as control variables. Gender was dummy coded (1 = male); level of education was coded as follows: 1 = did not graduate from high school; 2 = high school graduate/GED; 3 = some college or other post-high school education; 4 = completed a 4-year college degree; and, 5 = graduate work or professional training beyond a college degree. Well-density of the county of residence (1 = high well density) was also included in the multivariate models as a control variable. And, as in the above analyses, mode of data collection (1 = mail survey) was included as a control factor.

As shown in Table 4, the bivariate associations between level of familiarity with frac flowback wastewater treatment technology and each of the six safe possible uses of treated wastewater from hydraulic fracturing operations were positive and statistically significant. This indicated individuals with higher levels of familiarity with frac flowback wastewater treatment technology were more likely than those with lower levels of familiarity to agree that treated wastewater from hydraulic fracturing operations could safely be used for each of the potential purposes. The multivariate results indicated the addition of the control factors had very little effect on the nature or significance levels of the odds ratios for the familiarity with frac flowback

wastewater treatment technology variable. One association – between level of familiarity with frac flowback wastewater treatment technology and using treated wastewater for municipal uses – became nonsignificant.

An examination of the control factors indicated males, individuals with higher levels of education, residents living in high well-density counties, and mail survey respondents were significantly more likely than females, individuals with lower levels of education, residents living in low well-density counties, and telephone survey respondents to agree that treated wastewater from hydraulic fracturing operations could safely be re-used by gas and oil industry operators. Males were also significantly more likely than females to agree that treated wastewater from hydraulic fracturing operations could safely be used to irrigate farmland and for human consumption. Higher-educated persons were significantly more likely than their lower-educated counterparts to agree that treated wastewater from hydraulic fracturing operations could safely be re-used by gas and oil industry operators and be used for industrial purposes (e.g., manufacturing, etc.). Lastly, telephone survey respondents were significantly more likely than mail survey respondents to agree that treated wastewater from hydraulic fracturing operations could safely be used for both livestock and human consumption.[5]

[insert Table 4 about here]

5. Conclusions

What substantive insights can be drawn from these data given the preceding analyses? First, with respect to respondents' level of familiarity with the process of hydraulic fracturing – the controversial gas and oil well stimulation/completion practice that has increasingly dominated public discourse and the media – the results indicate a more or less symmetrical

distribution. Whereas two of every five respondents (40%) indicated having some level of familiarity with the process (scores 5 through 7 on the 7-point familiarity scale), roughly the same percentage (43%) reported being unfamiliar with this practice (scores 1 through 3 on the 7-point familiarity scale). This balanced response distribution was less pronounced when respondents' level of familiarity with hydraulic fracturing by county of residence (high well-density counties vs. low well-density counties) was examined. Although not a formal hypothesis, we believed there would be a difference in the level of familiarity between residents in areas with low and high levels of natural gas drilling activity; this was confirmed. Respondents living in the high well-density counties were more familiar with the process than their counterparts living in low well-density counties.

When we turn our attention to sources of and trust in information about fracturing-related processes, at least two observations are worth noting. First, respondents reported newspapers, the natural gas industry, conservation/environmental groups, and landowner groups/coalitions contributed more to their knowledge about hydraulic fracturing than did regulatory agencies, Cooperative Extension, university professors, or the film *Gasland*. The pattern of responses differed slightly when it came to whether or not respondents trusted those same sources of information. Conservation/environmental groups, newspapers, and landowner group/coalitions retained their designation as being in the top four sources of information, but the natural gas industry was replaced by university professors. Indeed, in terms of "trust," the natural gas industry was viewed as among the *least* trustworthy sources of information. According to these data, it appears that even though the energy industry is educating the general public on hydraulic fracturing, local citizens remain skeptical and continue to distrust it [24, 25]. Moreover, these data indicate that while university professors may not have contributed a great deal of

information to respondents' knowledge about hydraulic fracturing, respondents are likely to trust them when they do. Further, these data revealed the 2010 film *Gasland* contributed *least* to respondents' knowledge of hydraulic fracturing and was the *least* trusted source of information.

A second observation deals with the statistically significant difference uncovered between respondents from low well-density counties and those from high well-density counties with respect to two sources of information – the natural gas industry and regulatory agencies. As noted above, respondents living in the high well-density counties were more likely than those respondents living in the low well-density counties to report they gained some degree of knowledge about hydraulic fracturing from the natural gas industry and regulatory agencies, and that they were more likely than residents in the low-well density areas to trust these two sources of information to provide unbiased, factual knowledge on the hydraulic fracturing process. Based upon these findings, one could reasonably conclude both the natural gas industry and regulatory agencies are being proactive in the delivery of information on hydraulic fracturing in areas with increased drilling activity.

Other substantive findings dealt with respondents' level of familiarity with the management and disposal of frac flowback water in the Marcellus Shale, their awareness of technologies to remove contaminants from frac flowback wastewaters, and their level of agreement that treated wastewater from hydraulic fracturing operations could safely be used for selected purposes. Most respondents in our study were more unfamiliar than familiar with the management and disposal of Marcellus Shale frac flowback water as well as with the frac flowback wastewater treatment technologies. With respect to the latter topic, respondents living in the high well-density counties were more familiar with the frac flowback wastewater treatment technology than their counterparts living in low well-density counties. This result is

most likely due to the aforementioned finding showing respondents in high well-density counties having higher levels of familiarity with the process of hydraulic fracturing as a whole.

An investigation of respondents' beliefs that treated frac flowback could safely be used for six potential purposes indicated the overall pattern of results paralleled those in the extant literature on the perceptions of the general public about using reclaimed and/or recycled water [26, 27, 28] and desalinated produced water [13, 14]. These studies demonstrated that acceptance of/opposition to the use of reclaimed, recycled, and desalinated produced water varied directly with intimacy or degree of human contact.

Last, bivariate and multivariate logistic regression results revealed that an understanding of frac flowback wastewater treatment technology was associated with higher rates of perceived safe uses of treated wastewater from hydraulic fracturing operations. These findings mirrored and supported results of earlier research both on the association between familiarity with desalination technology and potential safe uses of desalinated produced water [13, 14].

6. Implications and Policy Recommendations

The production of shale gas has greatly increased over the past decade. Concomitantly, so have the anti-drilling/anti-fracing debates and grassroots social movements to ban the use of horizontal drilling and multi-state hydraulic fracturing, the two technologies primarily responsible for the development of these once written-off hydrocarbon reservoirs. Despite increased opposition from environmental organizations, concerned citizen groups, and anti-industry activists, as well as intensified scrutiny and possible oversight from federal, state, regional, and local governments, we do not envision a nationwide moratorium on the use of these

technologies to develop shale gas resources in the foreseeable future. Other researchers predict a similar scenario [9]. In Rahm's [9] summation:

> There is too much resource to be had, too much need to satisfy, and too much money to be made. The controversy will probably drive drillers toward discovery and use of non-toxic alternatives for fracking chemicals whenever possible. Fear of liability will impel this shift probably as much as the desire to avoid costly and time consuming conflict with opposition parties. Communities near shale gas plays will continue to be transformed by the drilling activities. Rural pastoral land will be littered with drilling rigs, pipeline will be laid, and 24-7 industrial operations will continue until the play is fully exploited. Urban populations that find themselves in the middle of shale gas plays will likewise see their communities transformed to accommodate the industry. The water resources the drillers need will be diverted from other uses to permit shale gas recovery.

While some might see Rahm's summation as extreme, much of her rationale seems plausible given current efforts to reduce and/or eliminate national dependence upon foreign energy sources. We, however, believe ignoring it is not done with impunity. To that end, based upon our findings, we propose the following recommendations to the energy industry, community leaders, government and regulatory agencies, environmental and non-governmental organizations, and other stakeholders.

First and foremost, open, honest, and full communication between/among all stakeholders is paramount. The energy industry must inform local residents, community leaders, government and regulatory agency personnel, environmental and non-governmental organization representatives, and other interested parties about the potentially *positive aspects* and *negative*

consequences of shale gas development. This includes providing accurate and transparent information about the chemical composition and water volumes used in frac fluids and part of frac flowback wastewaters. In turn, the various stakeholders must effectively communicate their concerns, fears, anxieties, and hopes associated with shale gas development to each other, the public, and the energy industry. Open, honest, and full communication can only increase objective, factual knowledge and, at the same time, reduce subjectively perceived knowledge rooted in rumors, inaccuracies, and/or ignorance.

Further, we strongly encourage industry to share more information about wastewater treatment technologies with government and regulatory officials as well as the general citizenry. A need exists for honest, unbiased dissemination of information on wastewater treatment technology, information on how industry is implementing such technologies to reduce the amount of freshwater used, and accurate data on the number of trucks on the roads. Moreover, all of this information must be cast in layman's terms – specifying what current technology **can** and **cannot** do.

In addition to disseminating information about these technologies, we recommend that industry organize outreach educational programs and field demonstration site visits of operating wastewater treatment technologies [12]. Indeed, some energy companies are currently actively organizing and leading tours of their drilling operations. Researchers working on wastewater treatment technologies must do the same. Anecdotal information from these drilling operation tours suggests they have been relatively successful in changing some of the extreme negative perceptions of skeptical individuals.

Finally, we encourage the creation and/or advancement of transdisciplinary research and outreach educational programs to address the vast array of issues surrounding the exploration,

drilling, and production of shale gases. The Environmentally Friendly Drilling Program (EFD), founded in 2005 and presently managed by the Houston Advanced Research Center (HARC), is one preeminent example [29, 30].[6] Through advanced research and outreach, the EFD program listens to and engages the general public and key stakeholders (e.g., university researchers, national laboratory scientists, industry actors, regulatory agency personnel, and non-governmental organization representatives), and transparently addresses any/all concerns through effective communication processes/strategies in an effort to effectively surmount the numerous technological, social, economic, and environmental issues associated with unconventional energy development.

Taken together, the results of this research, and suggested recommendations for their use, have the potential to inform policies associated with hydraulic fracturing and the management, disposal, and reuse of frac flowback waters. As suggested by these data, both the natural gas industry and regulatory agencies have been proactive in the delivery of information on hydraulic fracturing in areas with increased drilling activity. Findings from statistical analyses revealed respondents living in the high well-density counties were more likely than those living in low well-density counties to report they gained some degree of knowledge about hydraulic fracturing from the natural gas industry and regulatory agencies. Moreover, they were more likely to *trust* these two sources to provide unbiased, factual knowledge on the process. Given this information, a potential policy option at the federal, state, and local levels might be for governments to create and manage public-private partnerships that include, at the very least, various stakeholders from the natural gas industry and regulatory agencies. By creating interactive partnerships that consist of all parties associated with and impacted by hydraulic fracturing, a more informed and knowledgeable public will emerge. Doing this can have huge dividends in reducing the need for

large-scale public ad campaigns aimed at mitigating false and/or incorrect information about the hydraulic fracturing process.

Our data also suggest that while university professors may not have contributed a great deal of information to respondents' knowledge about hydraulic fracturing, respondents are likely to trust them when they do. Federal and/or state agencies could capitalize on this finding by making additional funds available to encourage university professors, particularly social science faculty, to become involved in scientific committees focused on policy-making in this area. At the same time, such efforts would generate new opportunities to foster basic and applied transdisciplinary research on the social and environmental issues associated with high-volume hydraulic fracturing. By encouraging such efforts, the energy industry could be at the forefront of transdisciplinary research, creating models of public scholarship by bringing together experts (i.e., engineers and bench, natural, and social scientists) and members of the general public who are committed to the successful resolution of many of the problems associated with exploration and extraction of this vital national energy resource.

As demonstrated, respondents believed treated wastewater from hydraulic fracturing operations could safely be used for selected purposes. At the federal level, additional funds might be made available to enable research, development, and demonstration of technologies to facilitate the treatment of frac flowback and produced waters. Government at all levels might provide market mechanism and incentives for the oil and gas operators to treat and reuse frac flowback and produced waters. Indeed, given the increased demands on our nation's water resources, government at all levels might require oil and gas companies treat and reuse frac flowback and produced waters in their operations. Doing so might serve as a model for other

water-dependent industries to pursue efforts to reclaim their wastewater and at the same time preserve clean water.

Finally, these data from the Commonwealth of Pennsylvania also confirm that familiarity with frac flowback wastewater treatment technology is associated with higher rates of perceived safe potential uses. Public-private partnerships to encourage augmentation of wastewater treatment technology and beneficial reuse at local, regional, state, and national levels should be accompanied by educational and outreach programs aimed at increasing knowledge of the technology and, as stated above, exactly what the specific technology can and cannot accomplish.

Footnotes

[1] Geologists differ in their estimates of the exact size and location of the Marcellus Shale region. The current research focused on the area defined by Bernstein Research as the Central Core and Tier 1 in Pennsylvania [15]. The Core and Tier 1 areas were defined in terms of depth, thickness, porosity, thermal maturity, and silica content of the shale – factors that play into the economics of the gas yield. In addition to the 20 counties so defined, Washington County was added to the sampling frame because of the high incidence of drilling that had already taken place there.

[2] Well density data (indicated in parentheses) were compiled on March 23, 2012. Counties included in the low well-density category were: Bedford (.1), Blair (1), Cambria (1), Cameron (4), Centre (5), Clearfield (11), Clinton (10), Indiana (5), Lackawanna (.4), Somerset (2), Sullivan (10), and Wayne (.5). The high well-density counties included: Bradford (93), Fayette

(24), Greene (75), Lycoming (42), Susquehanna (61), Tioga (65), Washington (69), Westmoreland (20), and Wyoming (27).

[3] Two thousand random telephone numbers were entered into a telephone bank. Of the 2,000 telephone numbers, 496 were unusable (393 were nonworking/disconnected/other; 43 were computer/fax lines; 60 were business lines/nonresidential). Hence, the usable telephone survey sample was reduced to 1,504. Of these, 400 individuals completed the survey, resulting in a 26.6% completion rate. Two hundred and five individuals answered their telephone and either refused initially (n=174), refused mid-survey (n=19), suspended their effort and agreed to finish the survey at a later time (n=8), or scheduled a callback (n=4). The remaining 899 telephone numbers were all dialed 10 or more times and ended with no answer or with various answering machine/voicemail connections.

[4] While far from ideal, a 27% response rate for a general population mail survey is not atypical. Despite efforts to increase responses through attention to survey length, form, content, and the employment of multiple mailings and various incentives, response rates have increasingly declined across time [18,19]. However, recent studies have challenged the presumption that low response rates imply inaccurate findings. Indeed, past and ongoing research suggests that findings of studies with low rates of response tend to differ little, if at all, from those with higher rates of participation [19,20,21,22,23].

[5] Odds ratios for the control variables are not shown in Table 4. Detailed results can be obtained by contacting the lead author.

[6] For more information on the EFD program, visit www.efdsystems.org.

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Table 1
Contribution made by eight sources of information to knowledge about hydraulic fracturing

Sources of information[a]	Overall respondents	Respondents from low well-density counties		Respondents from high well-density counties
		Adjusted mean values[b]		
Newspapers……	1.71 (n=795)	1.73 (n=397)		1.69 (n=398)
Natural gas industry……...	1.30 (n=794)	1.18 (n=397)	**	1.42 (n=397)
Conservation/environmental groups…….	1.21 (n=793)	1.17 (n=396)		1.24 (n=397)
Landowner groups/coalitions……	1.01 (n=794)	0.96 (n=395)		1.07 (n=399)
Regulatory agencies..…….	0.98 (n=791)	0.90 (n=394)	*	1.05 (n=397)
Cooperative Extension……...	0.67 (n=789)	0.61 (n=394)		0.72 (n=395)
University professors…….	0.65 (n=791)	0.61 (n=394)		0.70 (n=397)
Gasland (the film by Josh Fox)……	0.41 (n=786)	0.39 (n=390)		0.43 (n=396)

[a] Contribution of source of information was coded as: 0 = none; 1 = very little; 2 = some; and, 3 = a great deal.

[b] Mean values adjusted for differences in mode of data collection.

* Statistically significant difference at the $p \leq 0.05$ level in mean values between respondents from low well-density counties and those from high well-density counties.

** Statistically significant difference at the $p \leq 0.01$ level in mean values between respondents from low well-density counties and those from high well-density counties.

Table 2
Trust in eight sources of information to deliver unbiased, factual knowledge on hydraulic fracturing

Sources of information[a]	Overall respondents	Respondents from low well-density counties		Respondents from high well-density counties
		Adjusted mean values[b]		
University professors……..	1.57 (n=794)	1.61 (n=398)		1.53 (n=396)
Conservation/environmental groups…….	1.57 (n=792)	1.59 (n=395)		1.55 (n=397)
Newspapers……	1.56 (n=797)	1.58 (n=400)		1.55 (n=397)
Landowner groups/coalitions……	1.53 (n=796)	1.53 (n=399)		1.53 (n=396)
Regulatory agencies..…….	1.44 (n=795)	1.38 (n=399)	*	1.51 (n=396)
Cooperative Extension……...	1.43 (n=780)	1.50 (n=393)		1.37 (n=387)
Natural gas industry……...	1.32 (n=798)	1.23 (n=400)	**	1.42 (n=398)
Gasland (the film by Josh Fox)…….	0.80 (n=753)	0.81 (n=379)		0.79 (n=374)

[a] Trust in source of information was coded as: 0 = no trust; 1 = very little trust; 2 = some trust; and, 3 = great deal of trust.

[b] Mean values adjusted for differences in mode of data collection.

* Statistically significant difference at the $p \leq 0.05$ level in mean values between respondents from low well-density counties and those from high well-density counties.

** Statistically significant difference at the $p \leq 0.01$ level in mean values between respondents from low well-density counties and those from high well-density counties.

Table 3
Perceived safe potential uses of treated wastewater from hydraulic fracturing operations

Ways treated wastewater from hydraulic fracturing operations could safely be used:	Overall respondents	Respondents from low well-density counties		Respondents from high well-density counties
	Percentage "yes"[a]			
Re-use by gas and oil industry operators…..	81 (n=787)	77 (n=394)	**	85 (n=393)
Industrial use (e.g., manufacturing, etc.)..….	77 (n=787)	74 (n=395)		79 (n=392)
Municipal uses (e.g., watering of golf courses and city parks, etc.)……...	52 (n=788)	49 (n=395)		55 (n=393)
Irrigation of farmland……	31 (n=788)	30 (n=395)		33 (n=393)
Watering of livestock……...…….	19 (n=789)	19 (n=396)		20 (n=393)
People's drinking water……..……...	11 (n=785)	10 (n=393)		12 (n=392)

[a] Percentages adjusted for differences in mode of data collection.

** Statistically significant difference at the $p \leq 0.01$ level in proportions between respondents from low well-density counties and those from high well-density counties who indicated that treated produced wastewater from hydraulic fracturing operations could safely be used for selected purposes.

Table 4
Logistic regressions of potential safe uses of treated wastewater from hydraulic fracturing operations

		Odds ratios	
Ways treated wastewater from hydraulic fracturing operations could safely be used:	**n**	**Bivariate**	**Multivariate[a]**
Re-use by gas and oil industry operators……	782	1.32***	1.23***
Industrial use (e.g., manufacturing)……	782	1.19**	1.13*
Municipal uses (e.g., watering golf courses and city parks)……...	783	1.09*	1.07
Irrigation of farmland……..	783	1.21***	1.19***
Watering of livestock……..	784	1.20***	1.21***
People's drinking water……..	780	1.17**	1.16*

[a] Odds ratios computed controlling for gender, education, well-density of county of residence, and mode of data collection.
* $p \leq 0.05$ level.
** $p \leq 0.01$ level.
*** $p \leq 0.001$ level.

Produced-Water Pretreatment Field Testing: College Station, TX, 15 September 2010

H.J. Turin & E.J. Sullivan

Los Alamos National Laboratory (LANL) and Texas A&M University (TAMU) jointly conducted field tests of three different produced-water pretreatment systems at the TAMU Riverside Campus in College Station on September 15, 2010. This report details the field tests and results.

Analysis and Sampling Plan

An extensive chemical analytical plan required a complex collection protocol. Each individual water sample required six different sample containers; the different containers varied in size (from 40 mL to 1 L), material (HDPE plastic, clear glass, amber glass), headspace requirements (no headspace, shoulder-full), filtration requirements (no filtration, 0.45µ filtration), and preservative requirements (none, hydrochloric acid). Each sample was given a number in the form 100915-HHMM (15 September 2010 - collection time). The entire analytical and sampling plan is outlined in Table 1.

Field Logistics

J. Turin left Los Alamos for College Station the afternoon of September 14, 2010 (private vehicle to ABQ, commercial airline to HOU, rental car to destination), and spent the night in a motel near the TAMU campus. On the morning of September 15, 2010, he met with TAMU Professors Carl Vavra (Food Protein Research Center) and Dave Burnett (Global Petroleum Research Institute) at Cater-Mattil Hall, and set off for the Riverside Campus. There we joined the rest of the team: Keith McLeroy (Texas Engineering Extension Service), Frank Platt (Petroleum Engineering), and Bobby Woods.

LANL Pretreatment Apparatus

The LANL apparatus was designed and built at LANL TA-46, and shipped to College Station in preparation for this test. The apparatus (Figs. 1,2) is somewhat complex in order to be versatile and applicable to a wide variety of experimental conditions. Design features include varied parallel / serial column configurations, on-line backflush capabilities, and multiple monitoring and sampling locations.

For the present experiment, a relatively simple configuration was used. The treatment process involved two stages: a first stage consisting of two columns in series (C-1 and C-3, see Fig. 1) packed with surface-modified zeolite (SMZ), and a second single-column stage (C-5) packed with untreated zeolite. (The parallel treatment line (C-2 & C-4) was not used.) Backpressure in the system was monitored at gauges G-0, G-1, G-3, and G-5; flow was monitored at meters F-1, F-3, and F-5. (In steady state operation, all three flowmeters should agree; observed discrepancies point to meter malfunctions or errors.)

Column Packing

Prior to my arrival in Texas, Frank Platt and Bobby Woods had prepared the LANL apparatus by packing columns 1, 3, and 5. (Columns 2 & 4 were not used in this installation). Each active column was loaded first with a few inches of glass marbles, to cover the bottom plumbing fittings. The marbles in turn were covered with 2" of high-density garnet sand. The three columns were then ¾ filled with pre-washed zeolite material as follows:

- Column 1: Hexadecyltrimethylammonium (HDTMA) SMZ, 8-14 sieve size
- Column 3: HDTMA SMZ, 14-25 sieve size
- Column 5: Untreated zeolite, 14-40 sieve size

A packed column is shown in Fig 3.

The HDTMA SMZ was obtained from New Mexico Tech, and is described in greater detail by Ranck et al. (J. Environ. Engineering, V. 131, No. 3, March 1, 2005).

Feedwater Source

Frank Platt and Bobby Woods obtained approximately 500 gallons of oil-field produced water for the experiment. The feedwater was contained in two trailer-mounted tanks, alongside two initially empty tanks for experiment wastewater (Fig. 4). The water was obtained from a local produced-water disposal wellsite, and at the conclusion of the experiment the wastewater was returned to the same facility. The feedwater in the tank was observed to have a floating sheen, which was sampled by Keith McLeroy; all water used in the experiments was drawn from the bottom of the tank, below the sheen.

Experimental Procedure

TAMU personnel had previously set up an experimental test bed, shown schematically in Fig. 5. A variable-speed pump was used to pump feedwater first through a fabric bag filter to remove large particulates, and through the experimental treatment system, and finally into a waste tank. Flowmeters and sample ports enabled system monitoring. The system design enabled rapid substitution of different treatment systems. On September 15 three different systems were tested: a Mycelx 20" column, a Polymer Ventures 20" column, and the LANL zeolite packed columns system described above.

The experimental conditions were intended to compare the three different systems as directly as possible. The two commercial systems were operated as close to the manufacturer's recommended flow rates as possible (Mycelx @ 6 gpm, Polymer Ventures @ 2.8 gpm); the LANL system was operated at 1 gpm. In each case, 100 gallons of feedwater was treated; the test duration was calculated based on the observed flowrate.

Sample Collection

Both LANL (Jake Turin) and TAMU (Keith McLeroy) collected samples during the experiment. In general, the samples were collected in parallel; this report only details the LANL samples.

A single sample was collected of the untreated feedwater, two samples were collected of the treated effluent from the commercial columns (one each from the Mycelx and the Polymer Ventures column), and four different samples were collected from the LANL apparatus. Full sample details are provided in Table 2.

The two LANL duplicate samples (100915-1515 and 100915-1516) were collected at the end of the treatment system (Fig. 1, port V-52) after 100 gallons had been treated, and are directly comparable to the Mycelx and Polymer Ventures samples. One of the samples (100915-1425) was collected at the same port after only 50 gallons had been treated, and the final sample (100915-1520) was collected at an intermediate port (Fig. 1, port V-32) after SMZ treatment but before the C-5 polishing, again after 100 gallons had been treated.

Sample Preservation

At the completion of each sampling episode, the 1 L aliquot for 413 (acid) analysis was acidified with 1 mL of concentrated hydrochloric acid. All samples were placed in an iced cooler in the field, and transported to a walk-in cooler in Carl Vavra's laboratory at the end of the day.

Initial Visual Observations

All three treatments visibly reduced the turbidity of the feedwater, with the LANL system and the Polymer Venture column showing greater improvement than the Mycelx column. A comparison of untreated, Mycelx-treated, and Polymer Ventures-treated water is shown in Fig. 6.

Both of the commercial columns accumulated significant debris in the course of treating 100 gallons of feedwater. Fig. 7 shows side-by-side comparisons of a new and used column.

Back-Pressure Readings and Pressure Testing

During all of the tests, backpressure and pressure drops across the treatment equipment were recorded. Both of the commercial treatment columns exhibited excellent flow characteristics, with no measurable backpressure developing during the entire 100-gallon test.
Running at 1 gpm, the LANL apparatus developed a maximum backpressure of 12 psi (at G-0, fig. 1) and a maximum pressure drop of 6 psi (G-0 – G-5). At the conclusion of the treatments tests, we flow-tested the columns by increasing the pump speed. At its maximum, the pump produced a flow rate of 1.9 gpm against a backpressure of 20 psi and a pressure drop of 15 psi. For comparison, the apparatus was designed to handle up to 100 psi, suggesting that with a much higher flow rate would be safely achievable using a more powerful pump. Treatment efficiency may decrease as flow rate increases, so this is clearly an area for further testing.

Return to Los Alamos, Submittal to Analytical Laboratory

The following day (September 16), I retrieved all of the samples from Carl Vavra's cooler, checked labeling, prepared Chain-of-Custody forms, and packed the samples for transport to the appropriate laboratories (organic acid aliquots to LANL, all others to Envirotech). All sample were packed in coolers with blue ice refrigerants. Samples bound for Envirotech were dropped at FedEx in College Station the morning of September 16; samples bound for LANL were handcarried back to Los Alamos that afternoon via rental car, commercial plane, and private vehicle. FedEx delivered the shipped samples to Envirotech on September 17, and I personally delivered the LANL samples to Blossom Cordova (C-CDE) on September 17.

Health and Safety Issues

This field effort was conducted in compliance with Low-Hazard Integrated Work Document #IWD-C-CDE-0014-10, Rev. 0. PPE for both field operations and laboratory acid-handling included safety glasses, gloves, long pants, and closed-toes shoes. No unexpected conditions or events were encountered.

Analytical Results

The LANL water samples were analyzed for BTEX, total petroleum hydrocarbons (TPH), total oil and grease (TOG), total oil and grease - acidified (TOGA), and organic acids (OA). Results are presented in Table 3. All of these methods measure a portion of the organics in the system by using different extraction and cleanup methods. In general, the methods will be sensitive to different classes of organics as follows:

BTEX: volatile aromatic hydrocarbons
TPH (EPA 418.1): hydrocarbons
TOG (EPA 413.2): hydrocarbons, alcohols, phenols, ketones, aldehydes
TOGA (EPA 413.2): hydrocarbons, alcohols, phenols, ketones, aldehydes, C5+ organic acids

Because of the overlapping nature of the target classes, it is anticipated that results should be ordered TPH < TOG < TOGA. With few exceptions, this was observed (Table 3). (The unusually high TPH value for sample 100915-1515 was not replicated in the duplicate sample, and is likely a laboratory error.) All of these analytical methods tend to be sensitivity-limited near their detection limits, around 1 mg/L.

The organic acid analyses raised a couple of questions.

- Although the analysis identified acetic acid in all samples, a much larger chromatographic peak was detected at a retention time of 8.25 min, but has not yet been identified. Possible candidates include propionic, oxalic, and malonic acids; additional analytical work is underway.
- The acetic acid results do not seem internally consistent, and in fact the lowest and highest results reported, correspond to the two duplicate samples collected. These results are being reviewed.

Despite these lingering questions, it seems likely that low molecular weight organic acids (<C5) are indeed present in the samples, at concentrations on the order of 100 - 1000 mg/L. These light acids would not be detected in the BTX, TPH, TOG, or TOGA analyses, and are therefore not inconsistent with those results. It is not clear what classes of organics the NPOC (TEEX) analysis method (persulfate/UV oxidation, followed by CO_2 quantification) is sensitive to, so its agreement with the other methods is difficult to judge.

Discussion

The goal of the test was to compare different pretreatments for total organic removal effectiveness for example produced water. A secondary goal for LANL was to gain a better knowledge of the distribution of polar and nonpolar organic compounds in the produced water, because this distribution will affect the effectiveness of SMZ columns as well as other sorption-based pretreatments. All of the pretreatment materials used in this test rely on sorption (hydrophobic separation of nonpolar organics) as a removal mechanism, rather than chemical or physical (e.g., heat) destruction. Polar organic acids are not expected to be sorbed by any of the tested media.

Figure 7 shows the removal of the BTEX by the different pretreatment systems. These BTEX constituents are of regulatory interest and may be the highest concentration volatile organics in produced waters. Removal of total BTEX after 100 gal flow varied from 1 percent for the Mycelx column, to 1.5% for the Polymer Ventures column, to a range of 47% to 52% for the SMZ columns.

Our analytical data indicate that <C5 organic acids are the major fraction of organic carbon in these waters. This is consistent with published reports on the concentration ranges of organic acids in produced water [1]~~;~~ [2]). In comparison, ~~t~~total oil and grease (acidified or non-acidified) is a minor fraction (2-3 mg/L), as is total BTEX (~2.0 mg/L). None of the tested processes showed removal of oil and grease or TPH after 100 gal flowthrough. Because SMZ has been shown to be an effective sorbent for TPH and hydrophobic organic constituents [3, 4], the presence of the <C5 organic acids may positively skew the TPH and other results, as these constituents are not expected to be adsorbed.

None of these values were in the same range as non-purgeable organic carbon (NPOC) reported by TEEX (K. McLeroy, September, 2010, personal communication) for these waters. Ranges of the TEEX values were from 223-188 mg/L as NPOC. TEEX reported 10% removal of the fraction identified as NPOC by SMZ, but did not report (to LANL) removal percentages of any other processes.

Without more testing to identify specific compounds of concern, (alkanes, and aromatics) that may be sorptive it is difficult to define the effectiveness of the testing for nonpolar organics. In any event, these organics are of low enough concentration (1-4 mg/L) to be of minimal concern to reverse osmosis processes (RO) downstream, particularly as the TPH values were at 1 mg/L for most of the processes. Most membrane manufacturers recommend keeping organic content to a minimum (0.5-1.0 mg/L TOC) to prevent membrane fouling. This advice usually does not distinguish between types of organic classes, although it can be assumed to apply to both filming (surfactant) and nonpolar constituents at a minimum. Improved removal of nonpolar organics may be achievable by adjusting flow rates lower for the filter media, or changing the media more frequently. Clearly the SMZ

outperformed the prepackaged media, however, adjustments to flow rates or contact times may improve performance.

OAs may have a variable effect on membranes. At low concentrations, polar OAs can be consumed by microbes and enhance microbial growth and, thus, membrane fouling. At high concentrations (>100 mg/L), OAs can act as bacterial growth inhibitors (similar to acetic acid, or vinegar, in preservation of foods)-[5] .The effect of the high level of OAs detected here on downstream membranes needs to be determined for this system.

If further removal of OAs is needed, there are several options to enhance removal in the pretreatment phase. Acidification to pH 4 or less prior to pretreatment columns may improve adsorption, but will need further testing. Alternately, use of nano-filtration membranes at higher pH levels-[6] would likely remove almost all of the OAs in advance of RO membranes. Membrane bioreactors also have been proven to remove organic acids with nearly 100% effectiveness [7]. Adding a pretreatment to reduce this specific class of organics will likely be beneficial to any RO process.

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Species	Filter?	Preservative	Headspace	Container	Analyst
413-acid (Oil & grease, including organic acids)	None	1 mL conc HCl	Shoulder	1 L amber glass	Envirotech / Farmington, NM
413-neutral (Oil & grease)	None	None	Shoulder	1 L amber glass	Envirotech / Farmington, NM
418 (Total petroleum hydrocarbons)	None	None	Shoulder	1 L amber glass	Envirotech / Farmington, NM
Inorganics: • Major cations • Major anions • pH • Alkalinity • Iron	None	None	Shoulder	500 mL polyethylene	Envirotech / Farmington, NM
BTEX	None	Nitric	None	40 mL clear glass	Envirotech / Farmington, NM
Organic acids (unfiltered)	None	None	None	40 mL clear glass	Blossom Cordova / C-CDE
Organic acids (filtered)	Pressure	None	None	40 mL clear glass	Blossom Cordova / C-CDE

Table 1. Analytical and sampling plan.

Sample ID	Description
100915-1350	Pre-treatment water
100915-1105	Mycelx-treated water (after 100 gal)
100915-1145	Polymer Ventures-treated water (after 100 gal)
100915-1425	LANL-treated water (after 50 gal)
100915-1515	LANL-treated water (after 100 gal)
100915-1516	LANL-treated water (after 100 gal) - duplicate
100915-1520	LANL pre-polisher water (after 100 gal)

Table 2. Sample details.

Sample ID	Description	Benzene	Toluene	Ethyl-benzene	p,m-Xylene	o-Xylene	Total BTEX	TPH	TOG	TOGA	NPOC	Acetic Acid	Unknown (8.25)	TOGA-TOG
100915-1350	Pre-treatment water	0.784	0.820	0.053	0.248	0.143	2.050	1.0	1.8	2.7	223	123	1666	0.9
100915-1105	Mycelex: post-treatment	0.811	0.818	0.048	0.214	0.130	2.020	1.0	1.7	3.1	n/a	118	1527	1.4
100915-1145	Polymer Ventures: post-treatment	0.802	0.845	0.048	0.205	0.131	2.030	1.1	0.9	4.5	n/a	100	1608	3.6
100915-1425	LANL: post-treatment (50 gal)	0.400	0.082	0.001	0.005	0.004	0.491	1.0	1.9	3.2	195	117	1491	1.3
100915-1520	LANL: pre-polisher (100 gal)	0.704	0.346	0.003	0.012	0.012	1.080	2.0	0.9	3.4	n/a	95	1520	2.5
100915-1515	LANL: post-treatment (100 gal)	0.634	0.280	0.002	0.008	0.008	0.932	13.6 (?)	0.5	4.1	196	128	1629	3.6
100915-1516	Duplicate of 100915-1515	0.657	0.283	0.002	0.008	0.009	0.959	1.0	0.7	n/a	196	85	1342	n/a

Notes:

- All results are in mg/L.
- TPH: Total Petroleum Hydrocarbons; TOG: Total Oil & Grease; TOGA: Total Oil & Grease (acidified); NPOC: Non-Purgeable Organic Carbon.
- Unknown: organic acid peak with 8.25 min retention time; concentration calculated using oxalic acid calibration.
- n/a: not analyzed (sample lost or not collected).

Data Sources:

- BTEX, TPH, TOG, TOGA – Envirotech (Farmington, NM)
- NPOC – Keith McLeroy (TEEX)
- Organic Acids – Blossom Cordova (LANL C-CDE)

Table 3. Organic analysis results.

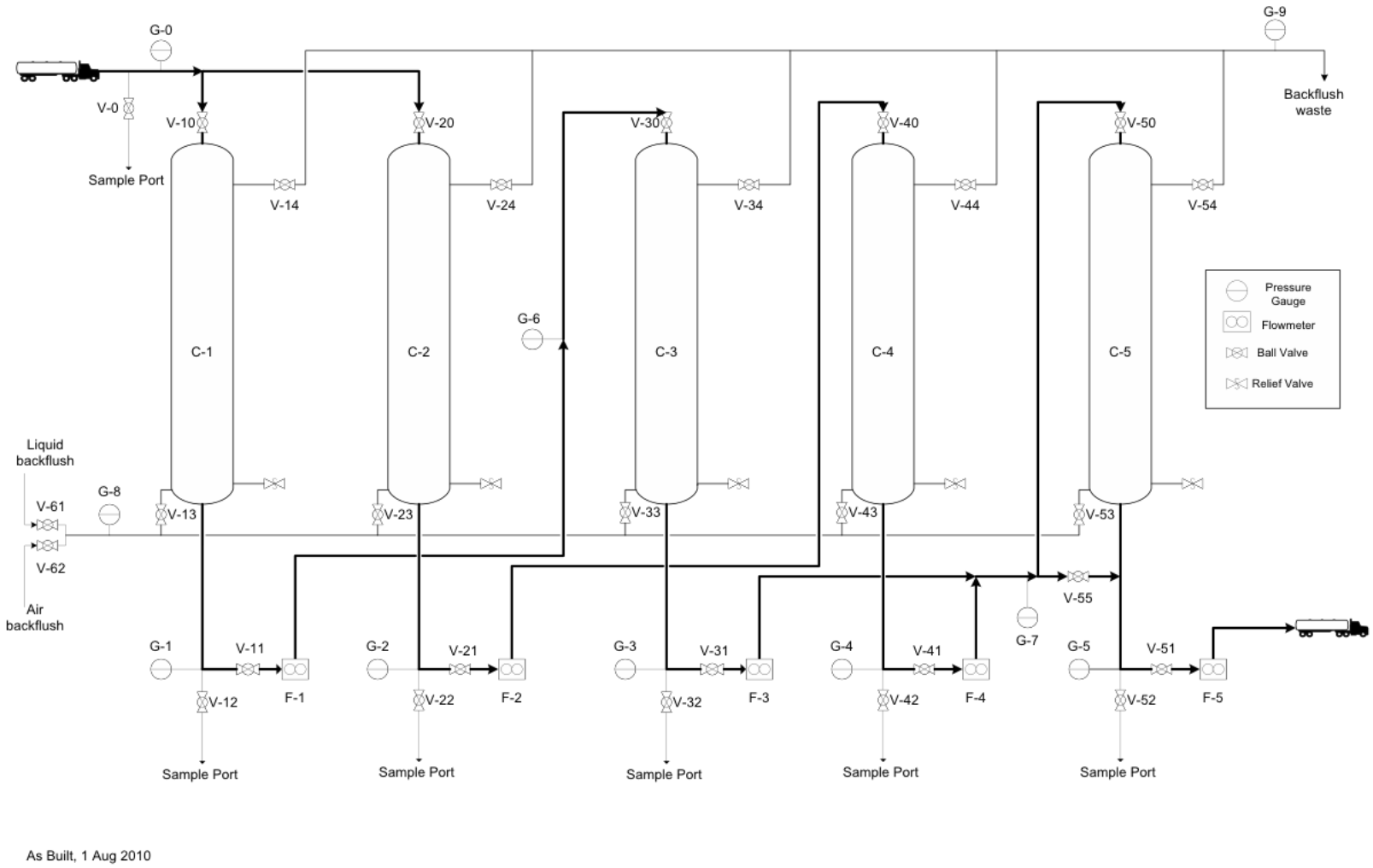

Fig. 1. LANL apparatus schematic

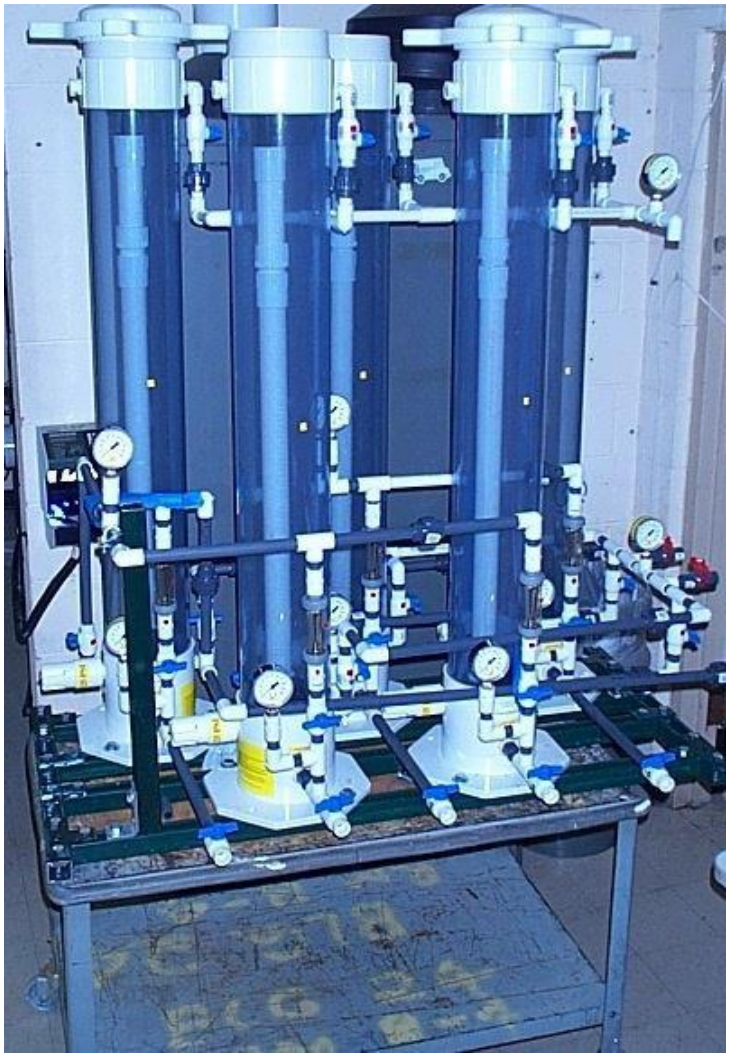

Fig. 2. LANL apparatus

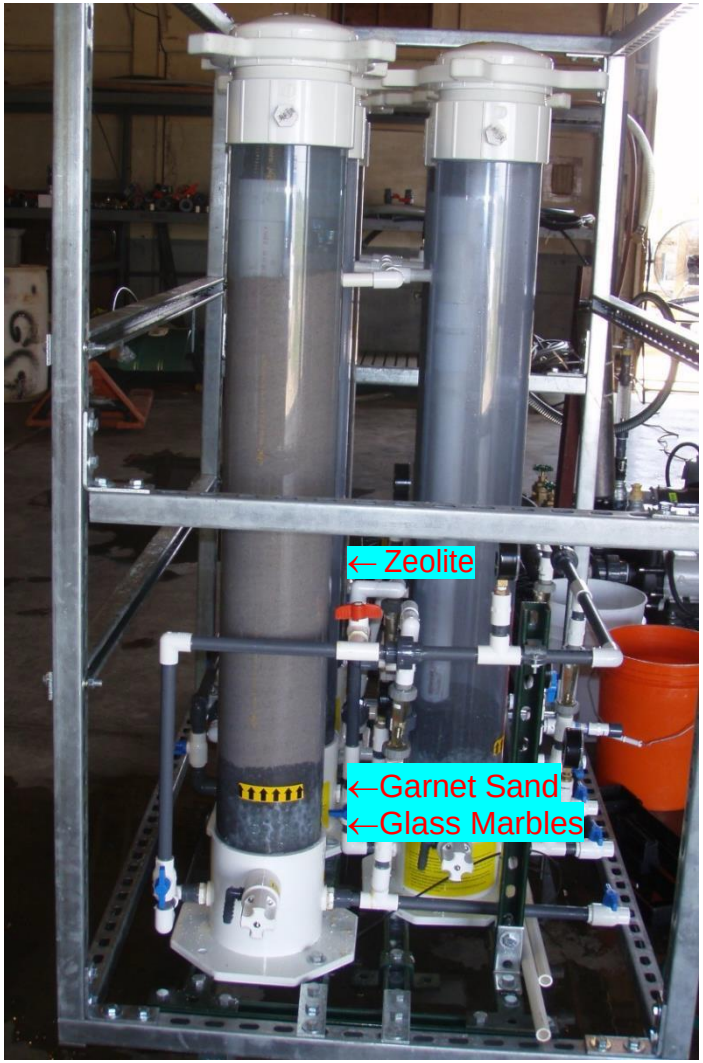

Fig. 3. Detail of LANL column packing

Fig. 4. Experimental setup, showing feed water tanks (back left), wastewater tanks (back right), variable speed pumps (on floor, foreground), pump controller (on top of plywood box), and bag filter (in metal canister, front foreground).

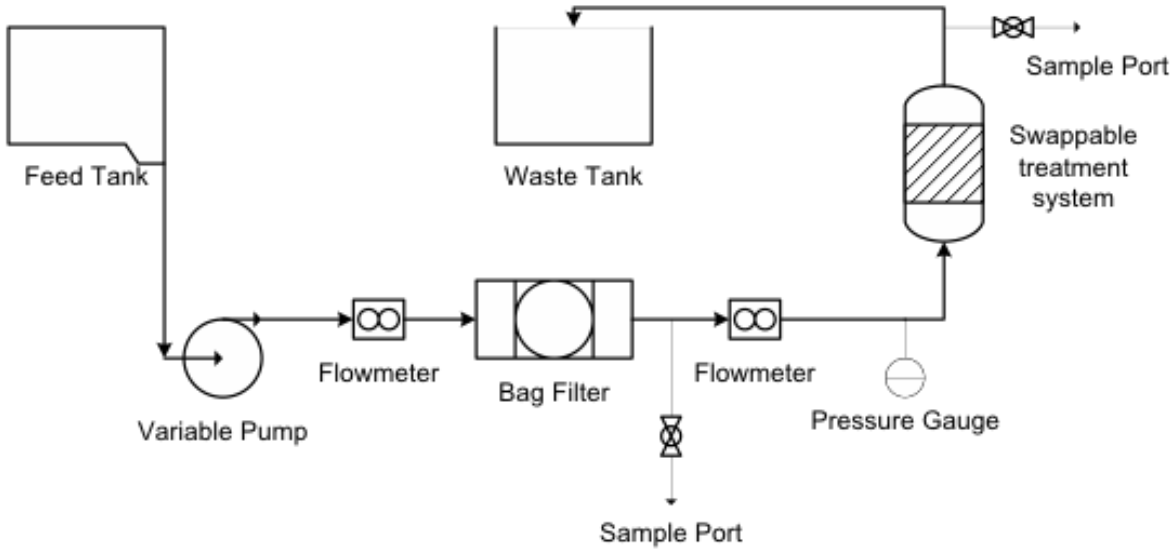

Fig. 5. Experimental setup schematic

Fig. 6. Comparison of untreated water (left), Mycelex-treated water (center) and Polymer Ventures-treated water (right).

Fig. 7. Comparison of new (left) and used (right) treatment columns, after treating 100 gallons of feedwater. Mycelx column, left photo, Polymer Ventures column, right photo.

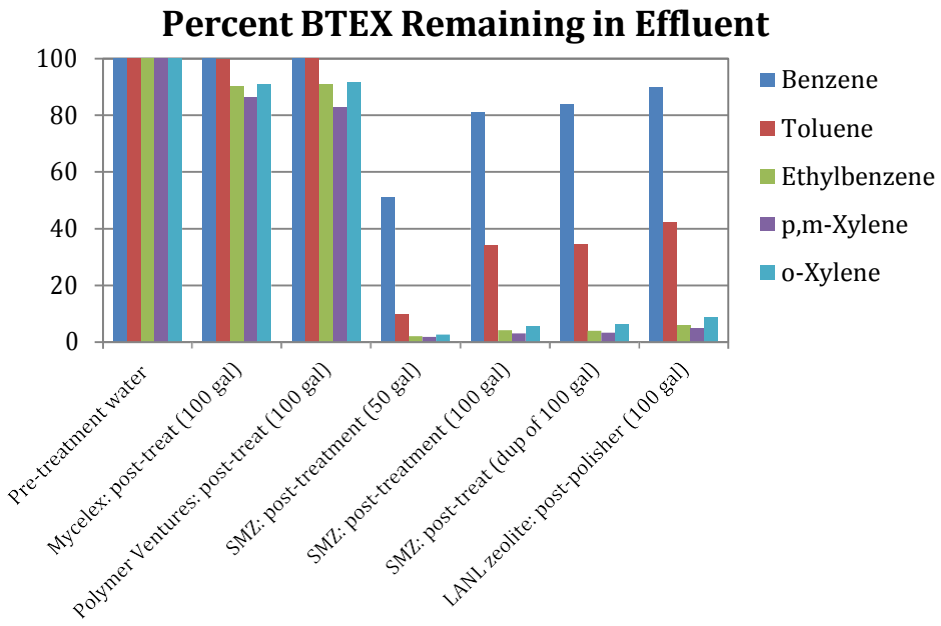
Percent BTEX Remaining in Effluent
100
80
60
40
20
0
Benzene
Toluene
Ethylbenzene
p,m-Xylene
o-Xylene
Pre-treatment water
Mycelex: post-treat (100 gal)
Polymer Ventures: post-treat (100 gal)
SMZ: post-treatment (50 gal)
SMZ: post-treatment (100 gal)
SMZ: post-treat (dup of 100 gal)
LANL zeolite: post-polisher (100 gal)

Figure 8. Benzene, Toluene, Ethylbenzene, and Xylenes remaining in effluent after each pretreatment.

Appendix B

Trip Report: Produced-Water Pretreatment Field Testing

College Station, TX, April 25 2012

Seth Steichen, E.J. Sullivan

Los Alamos National Laboratory (LANL) conducted field testing of a produced-water pretreatment apparatus with assistance from faculty at the Texas A&M University (TAMU) protein separation sciences laboratory located on the TAMU main campus. The following report details all of the logistics surrounding the testing.

Purpose of Test

The purpose of the test was to use a new, commercially-available filter media housing containing modified zeolite (surfactant-modified zeolite or SMZ) porous medium for use in pretreatment of oil and gas produced water (PW) and frac-flowback waters. The SMZ was tested previously in October, 2010 in a lab-constructed configuration ("old multicolumn system"), and performed well for removal of benzene, toluene, ethylbenzene, and xylenes (BTEX) from PW. However, a less-expensive, modular configuration is needed for field use. A modular system will allow the field operator to add or subtract SMZ filters as needed to accommodate site specific conditions, and to swap out used filters easily in a multi-unit system. This test demonstrated the use of a commercial filter housing with a simple flow modification and packed with SMZ for removing BTEX from a PW source in College Station, Texas. The system will be tested in June 2012 at a field site in Pennsylvania for treating frac-flowback waters. The goals of this test are: 1) to determine sorption efficiency of BTEX in the new configuration; and 2) to observe the range of flow rates, backpressures, and total volume treated at a given flow rate.

Field Logistics

S. Steichen left Los Alamos, NM on Wednesday April 18 (driving a government fleet truck) and stayed at a Hotel overnight in Wichita Falls, TX before arriving in College Station, TX and meeting with David Burnett (Global Petroleum Research Institute). On Monday April 23 he met

with Carl Vavra (Food Protein Research Center), and then left with Frank Platt (Petroleum Engineering) and Bobby Wood (TAMU Protein Separation Sciences) to the TAMU Riverside campus location to re-build the crate around an old multi column pretreatment unit and load it into the government truck. The following day was spent modifying the new pretreatment unit before executing the field testing on April 25 at Cater-Mattil Hall on the TAMU main campus.

LANL Pretreatment Apparatus

The column is a XL234B Modular Filter that was purchased from Filter Specialists, Inc (Figure 1).

Figure 1. Pretreatment apparatus with inflow at top and outflow at the bottom.

It stands upright with an inlet port near the top, and outflow port at the bottom. A removable top allows for access to the polypropylene felt bag, which contains the filter media (zeolite). The bag is 72.6 cm long with a circumference of 21.6 cm. The bag vessel is 75 cm tall (http://www.fsifilters.com/products.php?prod_id=34).

Column Packing and Modification

In order to improve flow through the filtration media (SMZ) the water was directed down the center of the bag filter by modifying the basic treatment system. A length of 3.8 cm diameter PVC pipe was cut to extend to the bottom of the bagged filtration media (72.6cm) and capped at the bottom end. Holes were then drilled around the circumference with increased frequency near the top to allow water flow throughout the column. A circle of plexi-glass was also cut to fit around the down tube, and was secured with rubber gaskets (Shown in Figure 2).

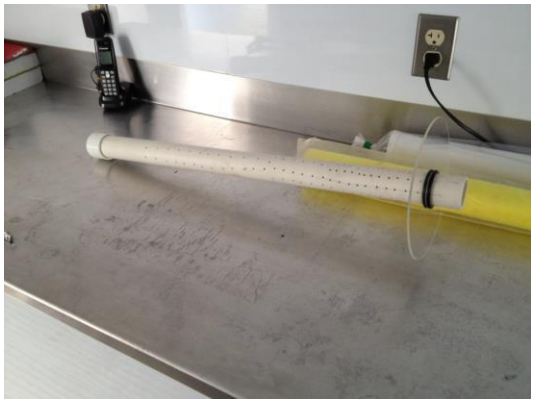

Figure 2. Completed modification ready to be installed into pretreatment apparatus (fabricated by Bobby Wood)

Figure 3. Tube installed in pretreatment apparatus filled with glass marbles and surrounded by 14-40 SMZ

The tube was then filled with glass marbles for stabilization and flow control and inserted into the apparatus, capping the top of the media bag (Figure 3). Surrounding this tube, the bag was filled with 14-40 sieve size surfactant modified zeolite (SMZ) brought from LANL. The SMZ was prewashed with city water prior to packing the column to reduce turbidity from fine particulates.

Feedwater Source

On the morning of April 25, Bobby Wood retrieved approximately 250 gallons of oil-field produced water from Advance Hydrocarbon Corporation, a disposal company located in College Station, TX. This tank, as well as an identical one for post treatment water containment, was situated next to the pumping station built into a TAMU trailer (Figure 4).

Figure 4. Source Water tank (left), post treatment water tank (right), Mobile treatment trailer (background). Picture taken at conclusion of experiment.

The trailer is designed as a mobile water treatment facility, and contains several variable speed pumps feeding a customizable treatment system capable of a variety of functions (low/high pressure, micro-nanofiltration). The water to be treated was observed to have a dark brown/rust color from outside the tank, with more of a green tint when sampled at a smaller volume. The source of the water is the same as was used for the previous test in October 2010, however, we note that PW is naturally variable and the water obtained for the current test was much higher in BTEX than previously.

Experimental Procedure

The source water tank was connected to a variable-speed pump which fed into a pretreatment bag filter intended to remove larger particles, then into the top of the LANL treatment apparatus, through the SMZ filtration media, and out into an empty water tank for proper disposal. The system contained built-in flow rate and pressure monitors at inflow and outflow points, and was controlled precisely from a computer system run on DASYlab software. The water was run through the system at several increasing rates (1.9 GPM, 3.1 GPM, and 3.8 GPM) and then brought back down to 1.9 GPM over a continuous period of time (15:00 to 16:25) in order to observe the effect of flow rate on the retention or break through of volatile organic compounds including BTEX.

Sample Collection

Bottle kits were sent directly to TAMU from Hall Environmental (Albuquerque, NM) prior to the test, and were used by LANL (Seth Steichen) to collect samples throughout the experiment. Three samples were taken during each increasing flow rate period (3x1.9 GPM, 3x3.1 GPM, 3x3.8 GPM) at roughly even intervals for BTEX and total organic carbon (TOC) analysis. Two more samples were collected during the return to the slower 1.9 GPM flow rate. All of these samples were collected at the point of the water flowing into the disposal tank outside of the trailer. One sample was taken at a sampling valve situated in-line before any filtration for the BTEX, TOC, and cation/anion analysis of the Source Water. All samples were analyzed during the experiment for pH, TDS, and turbidity using equipment set up inside of the trailer.

Sampling Method

Each sample was labeled with the gallons per minute flow rate followed by a number corresponding to the volume of water that had passed through the system at the time of sampling (ex; 1.9 GPM 13). These samples were all taken in 40 mL glass VOA vials with no head space. The vials were all pre-conditioned with HCl to preserve samples. One sample was taken from the untreated source water (labeled Source Water) and collected with the same sample containers as those mentioned previously in addition to; a 125 mL HDPE bottle preserved with HNO3 (filtered at 0.45 um, and filled to shoulder), a 500 mL non-acidified HDPE bottle (filled to shoulder), and a 125 mL HDPE bottle preserved with H_2SO_4 (filled to shoulder). The sampling plan is outlined in Table 1.

Table 1. Samples, filtration, preservation, and analytical laboratory.

Analyte	Filter?	Preservative	Headspace	Container	Analyst
BTEX	None	HCl	None	40 mL Voa's	Hall Environmental (Albuquerque, NM)
TOC	None	HCl	None	40 mL Voa's	Hall Environmental (Albuquerque, NM)
Cations	0.45 um	HNO_3	Shoulder	125 mL HDPE	Hall Environmental (Albuquerque, NM)
Anions	None	None/H_2SO_4	Shoulder	500/125 mL HDPE	Hall Environmental (Albuquerque, NM)

Sample Preservation

All of the bottles corresponding to species that required acidification (BTEX, TOC, cations, and partial anions) were pretreated with the proper type and volume of acid prior to arrival on site by Hall Environmental (Table 1).

Initial Visual Observations

The source water sample was a dark brown/rust color when observed in the large tank, but appeared to have more of a dark green color when observed in 1L aliquots for sampling from the pre-filtration port. This green tint was noticeably diminished in the post treatment samples at all flow rates, but remained throughout the test run. No precipitate was noted in the samples. If the samples were allowed to settle, then a sheen became visible on the top layer of the water. This is likely from oxidizing iron in the water. No foaming was noted in any part of the experimental set up. Foaming can indicate washoff of the SMZ surfactant.

Return to Los Alamos, Submittal to Analytical Laboratory

Following the experiment, all samples were labeled and placed with a corresponding chain of custody into a cooler with frozen blue ice. The cooler was kept overnight in a walk-in refrigerator at Cater-Mattil Hall before being shipped the next morning (April 26) to Hall Environmental for analysis. The government truck and old multicolumn pretreatment system arrived at LANL in the afternoon of the same day. The crate containing the pretreatment system was then taken into custody by Leon Lopez (LANL). The analytical results for volatile organics and field parameters are shown in Table 2. Additional analysis was performed on the source water for selected anions and dissolved metals (Table 3).

Table 3. Source Water Anions and Metals (all values reported in mg/L)

Fluoride	Chloride	Bromide	Phosphorus	Sulfate	Nitrate+Nitrite	Ca	Mg	K	Na
1.20	2900	12	<0.2325	2.6	<1	180	13	8.3	1100

Appendix B

Table 2. Analytical Results and Field Data

Sample	Time	pH	TDS (g/L)	Turbidity (NTU)	Benzene (µg/L)	Toluene (µg/L)	Elthylbenzene (µg/L)	Total Xylenes (µg/L)	1,2,4-Trimethylbenzene (µg/L)	1,3,5-Trimethylbenzene (µg/L)	TOC (mg/L)
Source Water	16:00	7.10	3.51	166	3300	7600	420	12000	3200	2100	140
1.9 GPM 13 gal	15:00	7.17	3.18	62.2	650	590	<5.57	440	130	98	86
1.9 GPM 30 gal	15:15	7.11	3.47	44.5	1300	1500	<5.57	1200	260	200	110
1.9 GPM 45 gal	15:24	7.07	3.68	76.6	2200	3100	110	3000	600	440	120
3.1 GPM 60 gal	15:31	7.15	3.65	83	2500	3900	140	4000	810	600	120
3.1 GPM 80 gal	15:37	7.14	3.52	69.3	2700	4400	160	4500	920	670	130
3.1 GPM 100 gal	15:43	7.12	3.63	84.1	2800	4700	180	5100	1100	780	130
3.8 GPM 115 gal	15:51	7.06	3.50	66.2	2900	5100	200	5700	1200	850	130
3.8 GPM 130 gal	15:55	7.03	3.49	71.9	3000	5900	200	5900	1200	840	140
3.8 GPM 150 gal	16:00	7.00	3.49	74.1	3000	5900	220	6400	1400	960	120
1.9 GPM 175 gal	16:14	6.99	3.50	64.8	3000	5800	230	6700	1500	1000	130
1.9 GPM 195 gal	16:25	6.99	3.50	50.6	2900	5000	170	5100	970	700	110

Health and Safety Issues

Close toed shoes, safety glasses, long pants, and gloves were used at all times during experiment and sampling phases of the trip. All work was done in accordance with guidelines expressed in the Integrated Work Documents entitled; Handling and Preparation of Field Water, Soil, and Algae Samples (IWD #: C-CDE-59-081111) and Field Water Sampling (IWD #: C-CDE-0014-10).

Results and Discussion

SMZ is used to remove sorbing, organophilic compounds from PW, including volatile organic compounds, semivolatile organics, waxes, oils, and colloidal organics. It is generally recognized as a regenerable porous medium that can be used similarly to other sorbents such as activated carbon and nutshells. It is resistant to chemical attack and microbial film accumulation and is tolerant of a wide pH range (2-12 pH units). Regeneration for volatile organics such as BTEX is accomplished by draining the column and air sparging.

Here, BTEX constituents were used as an indicator of treatment efficiency because their behavior in SMZ column systems is well understood. Benzene, in particular, is the least-sorbed of any of the organics of interest in PW. Thus, benzene breakthrough from a column is an early indicator that the column should be regenerated. SMZ columns have been shown to last for over 50 air-sparge regeneration cycles using PW, and increase in sorption efficiency and duration with each regeneration cycle.

Table 2 shows the analytical chemistry results from the test for each sample. Note that methyl tert butyl ether was analyzed, but not detected for any of the samples above the detection limit of 7.23 µg/L. Figure 5 shows the field parameter and total dissolved solids (TDS) results.

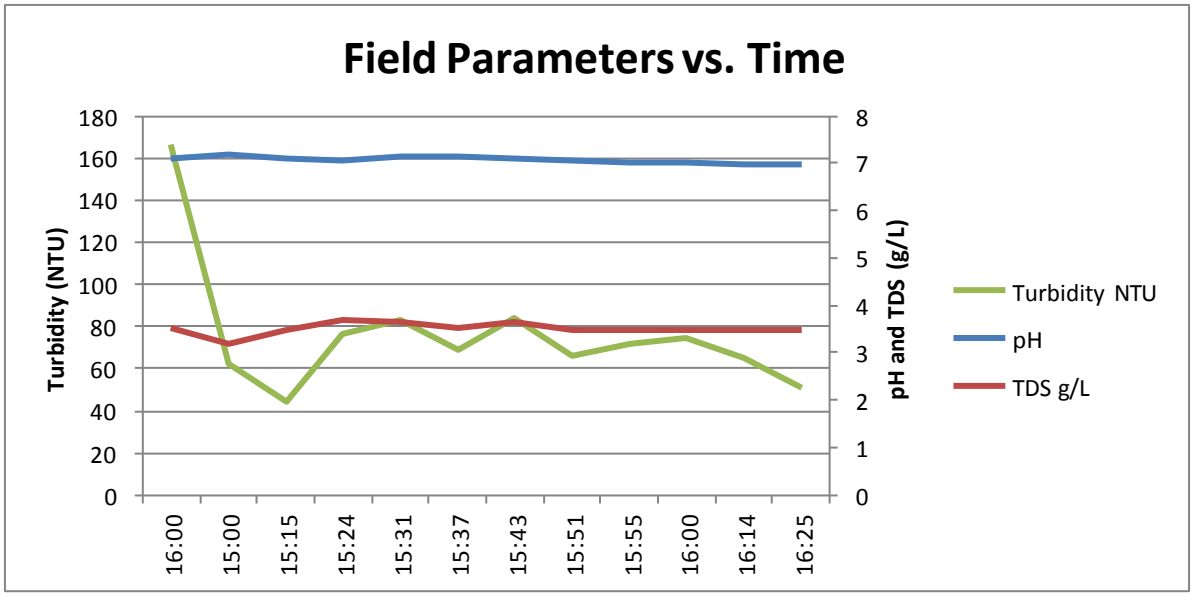

Figure 5. Field parameters over time.

Turbidity tends to be lower at low flow rates, similar to previous experiments. Turbidity has been shown to decrease with long term use of a column, as fines are removed. Backwash cycles are also useful in reducing turbidity further, or a microfilter following the column may be used. Total dissolved solids (TDS) change only slightly between samples; this is expected because SMZ is not intended to remove salinity. Here TDS is useful as an indicator of composition of the water treated. Total organic carbon is measured to give an overall indication of the organic content of the PW. PW contains a variety of sorbing (organophilic) and non-sorbing (hydrophilic) organic compounds. The sorbing compounds tend to include those of concern for toxicity (BTEX; semivolatile organics), while the non-sorbing compounds include organic acids (acetic, malonic) and alcohols (methanol, ethanol), among other compounds. Non-sorbing compounds may exist in much higher quantities than sorbing compounds, comprising the bulk of the TOC measurement, and may require further PW pretreatment to protect membrane desalination systems.

The first goal of the test was to determine the level of pretreatment achieved by the SMZ column for a given flow rate and total volume treated. Figure 6 shows the output concentrations of BTEX in µg/L and cumulative volume through the column versus time. Figure 7 shows this data as a ratio of C/C0 (output concentration/influent concentration).

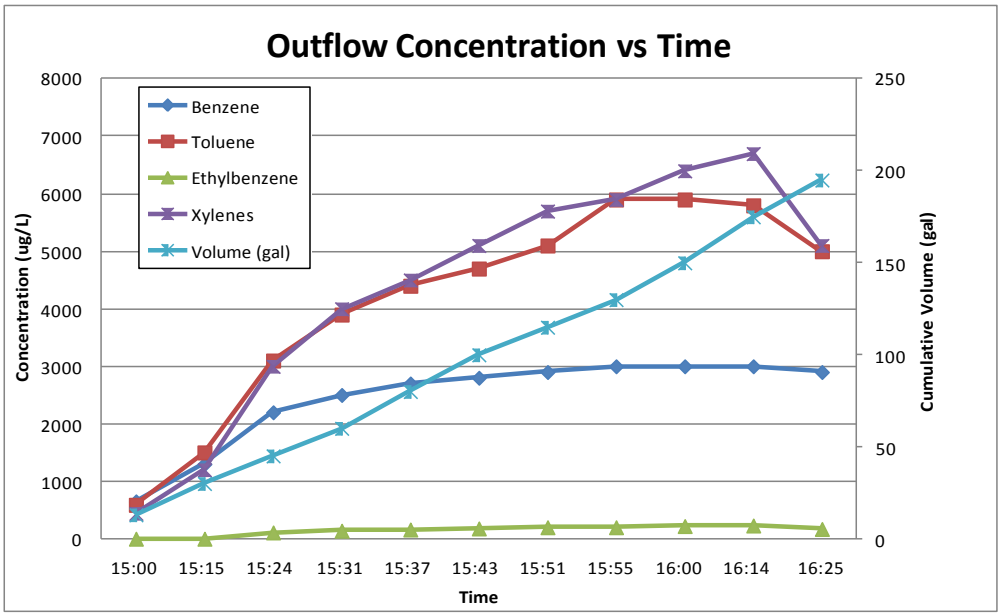

Figure 6. Concentrations of BTEX in post-column treated water in µg/L. Cumulative volumes of water passed through the column are shown on the right-hand axis.

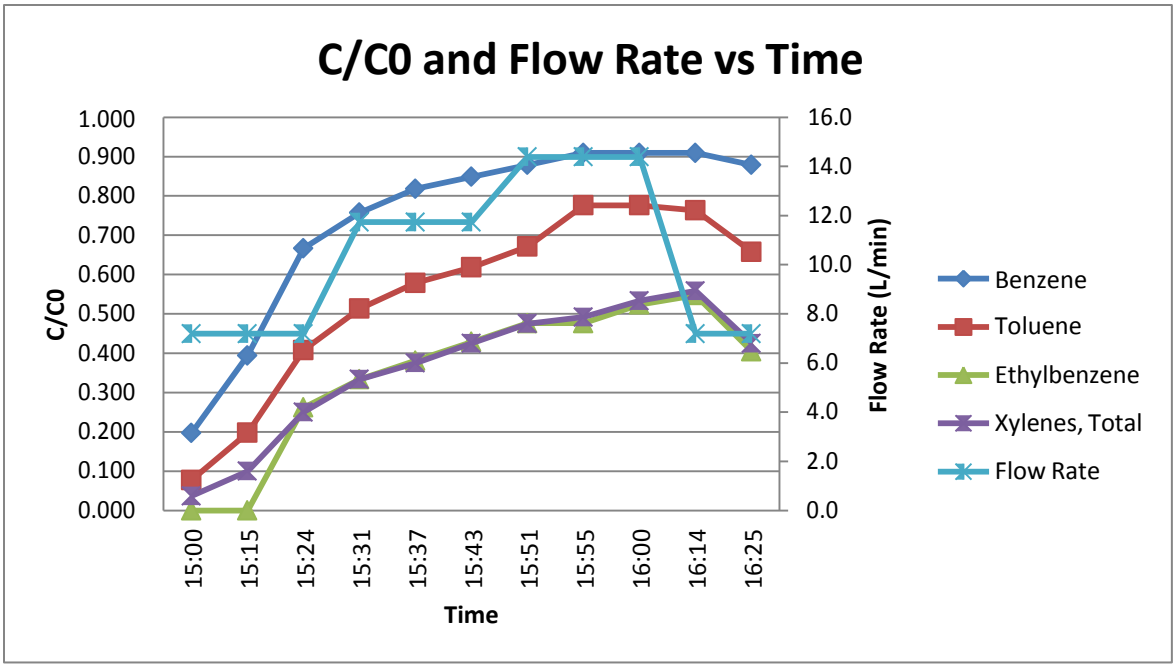

Figure 7. Outflow concentration/influent concentration (C/C0) for BTEX. Breakthrough occurs as the ratio reaches 1.0. Breakthrough was not observed in the timeframe of the test.

Full breakthrough (no further sorption) is achieved when C/C0=1. Because the flow rates varied, the curves are not smooth. Benzene comes closest to full breakthrough first, followed by toluene, ethylbenzene, and total xylenes, in order of most to least soluble. The trimethylbenzene compounds (not plotted) are similar to or less soluble than the xylenes. Typically these constituents sorb predictably in a linear sorption isotherm form [1]. Some dilution is likely to have occurred in the first sample retrieved at t=15:00, because the zeolite was initially wetted with tap water. A downward slope to the curves for the last, lower flow rate test indicate that sorption capacity was not fully used and that sorption is kinetically limited: e.g. sorption can be improved by optimizing the flow rate. Because total removal was not achieved, two or more columns would provide better removal and allow for air sparge regeneration without a flow interruption.

The second goal was to determine feasible flow rates for the column. The injection pressure was noted to be around 4 to 5 psi throughout the experiment, with little to no backpressure being indicated by the meters. The new zeolite offered very little resistance at the experimental flow rates. Further testing is needed to determine if fouling of the filter media over time has an effect on flow rate and pressure in the system.

Conclusions

A pilot-scale test of a commercially-available filter media support and SMZ for pretreatment of produced water showed good characteristics for a multiple-unit pretreatment system. Very high initial volatile hydrocarbon concentrations in the PW were reduced significantly by one column, addition of a second and possibly a third column would remove these constituents to a

low µg/L concentration in the outflow while allowing for air sparging regeneration. Modification of the commercial unit to improve flow likely shortened the flow paths for the PW in the column, while increasing dispersal in the media and reducing preferential flow paths. Reduced sorption was noted with increased flow rate; reducing the flow rate at the end of the test subsequently increased sorption, indicating that sorption is kinetically limited and that optimization of the flow rate to the goal output concentration will be needed depending upon water concentrations. Sorption was similar to previous tests conducted by Ranck et al. (2005).

Reference

1. Ranck, J.M., Bowman, Robert S., Weeber, Jeffrey L., Katz, Lynn E., Sullivan, Enid J., *BTEX Removal from Produced Water Using Surfactant-Modified Zeolite.* Journal of Environmental Engineering, 2005. **131**(3): p. 434-442.

Appendix C

Trip Report: Frac-Flowback Water Pretreatment Field Testing

Washington, PA, August 22-23, 2012
E.J. Sullivan

Los Alamos National Laboratory (LANL) conducted field testing of a produced water pretreatment apparatus jointly with faculty at the Texas A&M University (TAMU) mobile laboratory, located for this field test in Washington County, PA. The mobile lab is part of the Global Petroleum Research Institute (GPRI). The following report details the logistics surrounding the testing and includes test results.

Purpose of Test

The purpose of the test was to use a commercially-available filter media housing containing modified zeolite (surfactant-modified zeolite or SMZ) porous medium for use in pretreatment of frac flowback (FF) waters. The SMZ was tested previously in October 2010 in a lab-constructed configuration, and in April 2012 in the current configuration, both times for treatment of oil and gas produced water (PW). Previous tests were designed to remove benzene, toluene, ethylbenzene, and xylenes (BTEX) from PW. The current modular system is designed for field use and can be used in multiple configurations in parallel or series with standard fittings. This allows the field operator to add or subtract SMZ filters as needed to accommodate site-specific conditions, and to swap out used filters easily in a multi-unit system. This test demonstrated the use of the commercial filter housing with a simple flow modification and packed with SMZ to be used with FF source in Washington, PA. The goals of this test are: 1) to determine performance of the SMZ and filter housing with FF waters, and 2) to observe the range of backpressures encountered over a 2 gpm, 1000 gallon total volume flow test.

Field Logistics

E.J. Sullivan left Los Alamos, NM on Tuesday, August 21, 2012 and flew to Pittsburgh PA. She met TAMU personnel at the John Day well site in Washington County, PA on Wednesday, August 22 to begin field testing. TAMU personnel included Carl Vavra, Frank Platt, Bobby Wood, and Mark Adams. The well site is operated by Range Resources. Field setup was performed in the morning and flow testing was run from 1200 to 1700 hrs on August 22, and from 0830 to 1200 hrs on August 23.

LANL Pretreatment Apparatus

The column is an XL 234B Modular Filter that was purchased from Filter Specialists, Inc. (Figure 1). It stands upright with an inlet port near the top and outflow port at the bottom. A removable top allows for access to the polypropylene felt bag, which contains the SMZ media. The bag is 72.6 cm long with a circumference of 21.6 cm. The

bag vessel is 75 cm tall (http://www.fsifilters.com/products.php?prod id=34). Images of the top of the SMZ in the filter container are shown in Figures 1 and 2 (before and after the test). Some settling of the SMZ occurred during packing and testing.

Column Packing and Modification

The unit tested was previously used in a field test at College Station, TX in April 2012. The system was modified to improve flow characteristics at that time, and is described in further detail in the previous trip report LA-UR-12-21661. The same configuration and SMZ material was used for this test. Between tests, the SMZ was double rinsed with tap water and was removed from the bag and spread out to air dry, then repacked in the bag and the housing for transport. This drying is expected to remove any volatile organic compounds remaining sorbed to the media, although this was not verified for this test. Some settling of the material was observed during transport. The top of the media was observed to be about 1" below the bag handles prior to the start of the testing (Figure 2).

Feedwater source

The John Day well site houses eight unconventional (fracture-flowback) gas wells on a central pad, 6 produced water and oil storage tanks, and a large, 49 acre-foot capacity lined, aerated storage pond located on the hill approximately 100 feet above the pad elevation. The water is used by other sites for drilling and fracturing. This pond water, derived from the flowback gas wells, was used for the treatment test. This water is significantly different in chemistry from previous tested produced waters. Initial chemistry data was obtained from TAMU and is shown in Table 1. By observation the water is highly oxidized, with enough oxidized iron content to create a bright rust-orange color. Field parameters measured at the site are given in Table 2. The pH is lower than many produced waters (~6 pH units) and it is approximately 90,000 mg/L total dissolved solids (TDS). There is little to no BTEX in the water, but some organic carbon does exist. The water is stored in a large steel storage tank adjacent to the trailer prior to treatment. It is moved from the pond by pumping to the highest head point then gravity drains to the tank through 4" OD diameter black poly tubing. It was observed that each wellhead had a chemical additive tank, however, no access to the wellheads was obtained to determine what the additives were, or if they were being used at this time. Given the initial information about the water, the SMZ column was not expected to be effective for BTEX removal, but could still be tested for semivolatile organic removal, reduction of TOC and turbidity (due to removal of iron floc), and physical characteristics including flow capacity over time.

Health and Safety issues

Closed-toe shoes, safety glasses, fire-retardant long pants and long-sleeved shirts, and gloves were used at all times at the field site. Outdoor work also required a hard hat. All

work was done in accordance with guidelines expressed in the Integrated Work Documents entitled: “Handling and Preparation of Field Water, Soil, and Algae Samples” (IWD #: C-CDE-59-081111), and Field Water Sampling (IWD #: C-CDE-0014-10).

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Table 1. Frac Flowback water data provided by site operator (Range Resources).

Sample Data from Range Resources		**3/1/12**	
Analyte	**Result, units**	**John Day Impoundment**	**Weimer Produced Water**
Physical properties			
TDS	mg/L	93,000	143,000
pH		6.89	7.04
TOC	mg/L	102	98.2
Oil and grease	mg/L	35	20.2
BTEX	ppb	ND	ND
Hardness as CaCO3	mg/L	18,700	65,800
Turbidity	ntu	175	
Heterotrophic Bac-T	No growth		
Major Ions			
Chloride	mg/L	38,700	120,000
Calcium	mg/L	6,500	23,100
Magnesium	mg/L	632	2,180
Potassium	mg/L	224	355
Sodium	mg/L	16,600	44,800
Sulfate	mg/L	89	79
Sulfite	mg/L	1	1
Boron	mg/L	9	18
Silicon	mg/L	8	9
Silica	mg/L	16	19
Nutrients			
Nitrogen as Ammonia	mg/L	48	140
Metals			
Barium	mg/L	252	322
Iron	mg/L	17.5	97.1
Manganese	mg/L	3	7
Strontium	mg/L	9.7	9.88

ND: no lower detection limits provided

Appendix C

Table 2. Field Parameters collected by TAMU

TAMU Sample No.	LANL Sample No.	Sample date	Time	Description	TDS (g/L)	Cond (ms/cm)	Turbidity (NTU)	Fe (mg/L)	TOC (ppm)
SP-24	**A-1209**	Aug 22, 2012		Inflow	122.9		89	21.7	148
SP-25	**B-1209**	Aug 22, 2012		After Mycelx	116.1	198.9	75.8	23.3	139
SP-26	**C-1209**	Aug 22, 2012		After LANL	118.6	204.4	75.8	27.3	138
SP-27		Aug 22, 2012	1420	Inlet	119.4	205.7	111	30.6	136
SP-28		Aug 22, 2012	1420	After Mycelx	109	189.7	76	27.4	132
SP-29	**C-1615**	Aug 22, 2012	1420	After LANL	116.6	197.4	69.7	25.2	131
SP-30		Aug 22, 2012		Inflow	117.7	200.2	99.1	32.3	137
SP-31		Aug 22, 2012		Mycelx	120	205	69.4	26.7	125
SP-32		Aug 22, 2012		After LANL	119.7	206.3	67	25.1	123
SP-33	**A-0930**	Aug 23, 2012	935	Inlet	119.9	187.2	112	32.7	134
SP-34	**B-0930**	Aug 23, 2012		After Mycelx	117.6	186.8	89.5	31.6	133
SP-35	**C-0930**	Aug 23, 2012		After LANL	117.2	184.4	82.6	30.1	122
SP-36	**A-1145**	Aug 23, 2012		Inlet	121.5	204.7	111	33	133
SP-37		Aug 23, 2012		After Mycelx	120.3	204.4	111	33	131
SP-38	**C-1145**	Aug 23, 2012		After LANL	117.5	194.7	96.9	32.6	126

Experimental Procedure

The source water tank was connected to a variable-speed pump which fed into a Cetco 10 micron bag filter, followed by a Mycelex cartridge filter (pre-used with the same water at 1000 gallons flowed through prior to use on this test). The water then fed into the top of the SMZ unit, flowed through the SMZ media, and was discharged to the disposal water tank. The system contained built-in flow rate and pressure monitors at inflow and outflow points, and was controlled precisely from a computer system run on DASYlab software. Sampling ports A, B, and C were set up to allow sampling before the Mycelex and after the Cetco bag (port A), after the Mycelex and before the SMZ unit (port B), and after the SMZ unit (port C) (Figure 1). According to Mr. Vavra, the Cetco bag is to remove gross particulates, the Mycelex is to remove oil and grease and is “not good for BTEX”. Another Cetco bag was put in place after the SMZ unit in order to catch any washoff or degraded particles from the filter. Because SMZ is primarily used to remove BTEX, this test was determined to be mostly for testing physical properties of the filter under higher volumes (1000 gallons throughput), and to determine if it would remove other organics, particulates or iron from the water at a 1.9 gpm flow rate. The system was run at 1.9 gpm from 1150 hrs on August 22 until 1702 hrs, then restarted at the same flow rate on August 23 at 0840 hrs until 1202 hrs.

Figure 1. Schematic of sampling points.

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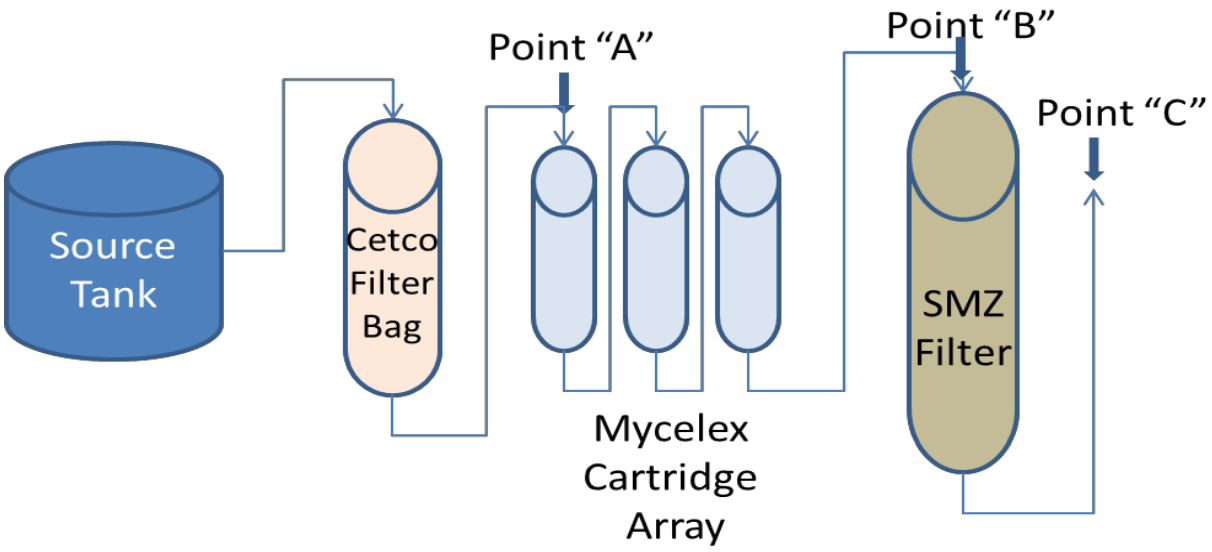

Sample collection, plan, and preservation

Bottle kits were sent directly to the site from Hall Environmental (Albuquerque, NM) prior to the test, and were used by Dr. Sullivan (LANL) to collect samples throughout the experiment. Samples were taken approximately every 2 hours on both days. TAMU also analyzed field parameters and HACH reactive Fe for each sample set, and recorded pressure profiles for the column. The sampling plan is shown in Table 3. "Hold" samples for BTEX and TOC were taken along with two sets incorporating additional parameters of interest for frac flowback waters, including cation/anion balance, organic acids, surfactants, and PAHs. Field parameters from TAMU are shown in table 2, and sample results from Hall are shown in table 3. Field parameters from LANL are also shown in Table 4. The number of gallons run through the system at each sample time is also shown. Samples were designated "Hold" for BTEX, because it was unknown if BTEX was present at the site. If the initial sample for BTEX from the pond was found to contain BTEX, then the later post-treatment samples would be analyzed.

VOA (BTEX) and TOC samples were taken in 40 ml glass vials pre-preserved with HCl. PAHs were taken in 1L amber jars and cation/anion balance samples were taken in 500 ml plastic bottles, non-preserved, or preserved with HNO_3 or H_2SO_4. Surfactants, gross alpha and beta, and organic acids (Volatile fatty acids or VFAs) were taken in plastic bottles and a set of two VOC vials preserved with H_2SO_4.

Initial Visual Observations

The source water sample was a reddish brown color, which was slightly reduced by treatment with the SMZ column. Samples preserved with H_2SO_4, taken before and after the SMZ column, were observed to generate a large amount of white precipitate (Figure

2). No hydrocarbon sheens or odors, and no sulfide-type ("rotten egg") odors were noted from any of the waters.

Table 3. **Samples, filtration, preservation, and analytical laboratory.**

Analyte	Filter?	Preservative	Headspace	Container	Analyst
BTEX	None	HCl	None	40 mL Voa's	Hall Environmental (Albuquerque, NM)
TOC	None	HCl	None	40 mL Voa's	Hall Environmental
PAHs	None	Ice 4°C	Shoulder	500 mL HDPE	Hall Environmental
Surfactants	None	Ice 4°C	Shoulder	500 mL HDPE	Hall Environmental (Albuquerque, NM)
Volatile Organic Acids	None	Ice 4°C	Shoulder	500 mL HDPE	Hall Environmental
Major Cations and metals	0.45 um	HNO_3	Shoulder	125 mL HDPE	Hall Environmental LANL
Anions	None	None/H_2SO_4	Shoulder	500/125 mL HDPE	Hall Environmental

Two additional samples were requested from the field site crew, to send directly to LANL for further testing of the white precipitate (Figure 4), and for total and dissolved metals analysis and acid effects. The colloidal iron was fouling the UF filters used for subsequent tests, and acidification tests were done at LANL to determine if the colloids could be dissolved to prevent fouling in the field. SEM/EDAX analysis of the precipitate was performed to determine gross composition (Addendum 1). It is most likely that the precipitate is gypsum ($CaSO_4$) from combination of the high sulfate concentration in the acid and dissolved calcium in the water. Acidification with both HCL and H_2SO_4 to pH 2 did remove the iron floc in solution.

Return to Los Alamos, submittal to analytical laboratory

Following the experiment, all samples were labeled and placed with a corresponding chain of custody (attached) into two coolers with wet ice bags. The cooler was shipped from Washington, PA on August 23 and arrived on the morning of August 24 at Hall Environmental in Albuquerque, NM. At Hall labs, samples were selected for analysis and

other samples placed on hold pending the first results. Results from the selected samples are shown in Table 4.

Results and Discussion

Flow rates and desired system pressures were maintained during the 2 gpm, 1000 gallon flow test. The lack of pressure drop across the media column indicated that no system fouling occurred. Analytical results (Table 4) show that, as expected, no BTEX removal was obtained during the current test, although less soluble semivolatile organic compounds, including acenaphthene, benzyl alcohol, pentachlorophenol, phenanthrene, and phenol, were significantly reduced or removed. The lack of BTEX removal stems from the reuse of the SMZ from a previous test, and the low levels of hydrocarbons in the starting water. Note that the use of the used SMZ was not specified by LANL; fresh or completely regenerated SMZ is always recommended for field tests. The lack of removal also indicates that the current design configuration provides insufficient residence time (or too short a flow path) for the more soluble organic constituents to be removed. The effective residence time for these systems should be measured using non-reactive tracers (such as bromide) to determine the best system design. Residence time can be increased by increasing the number of units in series, or by slowing the flow rate through each unit. Altare et al. [1] give design parameters, including empty bed contact times (EBCTs) for SMZ column sizing based on nonreactive tracer testing, zeolite grain sizes, and multiple regeneration steps. This information can be used to design an effective column setup using the new modular configuration, which is easier to handle in the field than the experimental designs used in previous tests.

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Table 4. Results from selected samples.

LANL Sample No.		A-1209	B-1209	C-1209	C-1615	A-0930	B-0930	C-0930	A-1145	C-1145	Trip Blank
Date Collected		8/22/12	8/22/12	8/22/12	8/22/12	8/23/12	8/23/12	8/23/12	8/23/12	8/23/12	8/24/12
Time		12:09	12:09	12:09	16:15	9:30	9:30	9:30	11:45	11:45	9:00
EPA METHOD 8021B: VOLATILES	units										
Methyl tert-butyl ether (MTBE)	ug/L	<1.4460	<1.4460	<1.446	<1.4460	held	held	held	<1.4460	<1.4460	<1.4460
Benzene ug/L	ug/L	3.5	2.9	3	2.9	held	held	held	3	2.9	<0.1413
Toluene ug/L	ug/L	5.9	7.2	14	13	held	held	held	8.2	12	<0.1183
Ethylbenzene ug/L	ug/L	3.1	3.8	5.5	5.4	held	held	held	3	4.5	<0.1114
Xylenes, Total	ug/L	11	11	13	13	held	held	held	13	14	<0.3315
1,2,4-Trimethylbenzene	ug/L	7.7	6.3	7.6	8.5	held	held	held	10	10	<0.1156
1,3,5-Trimethylbenzene	ug/L	4.7	4	4.6	5.2	held	held	held	6.8	6.3	<0.1111
EPA METHOD 9060 TOC											
Total Organic Carbon	mg/L	150	150	150	150				150	150	
EPA METHOD 300.0: ANIONS											
Fluoride	mg/L	<3.8053			<3.8053						
Chloride	mg/L	74000			78000						
Bromide	mg/L	860			880						
Nitrate+Nitrite as N	mg/L	<100.00			<100.00						
Phosphorus, Orthophosphate (As P)	mg/L	<30.370			<30.370						
Sulfate	mg/L	<11.790			<11.790						

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Table 4, continued			
EPA METHOD 200.7: METALS			
Calcium	mg/L	13000	13000
Iron	mg/L	34	30
Magnesium	mg/L	1300	1300
Potassium	mg/L	310	330
Sodium	mg/L	30000	31000
EPA 120.1: SPECIFIC CONDUCTANCE			
Conductivity	umhos/c	230000	240000
SM2540C MOD: TOTAL DISSOLVED SOLIDS			
Total Dissolved Solids	mg/L	144000	139000
SM2320B: ALKALINITY			
Bicarbonate (As CaCO3)	mg/L	23	24
Carbonate (As CaCO3)	mg/L	<2.000	<2.000
Total Alkalinity (as CaCO3)	mg/L	23	24
EPA METHOD 8270C: SEMIVOLATILES*			
Acenaphthene	ug/L	17	<13.256
Benzyl alcohol	ug/L	430	48
Bis(2-ethylhexyl)phthalate	ug/L	28	21
2,4-Dinitrophenol	ug/L	30	28
4-Nitroaniline	ug/L	16	14
Pentachlorophenol	ug/L	25	<8.1723
Phenanthrene	ug/L	17	<10.616
Phenol	ug/L	91	<12.583
*** Not all semivolatiles analyzed for are listed -- there was a significant number of semivolatiles ND**			

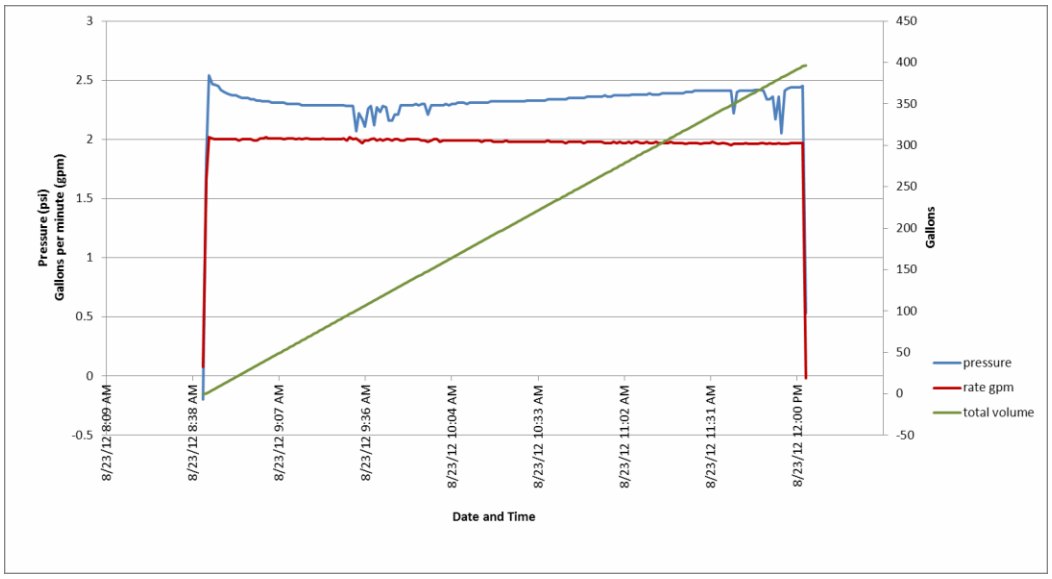
Appendix C

Figure 1. Zeolite in top of filter container, pre-test.

Appendix C

Figure 2. Zeolite in top of filter container, post-test.

Figure 3. Pressure, flow rate, and cumulative volume passed through the SMZ column with time.



Appendix C

Figure 4. Iron-oxide stained sample water and precipitate from H_2SO_4-acidified water at field site.

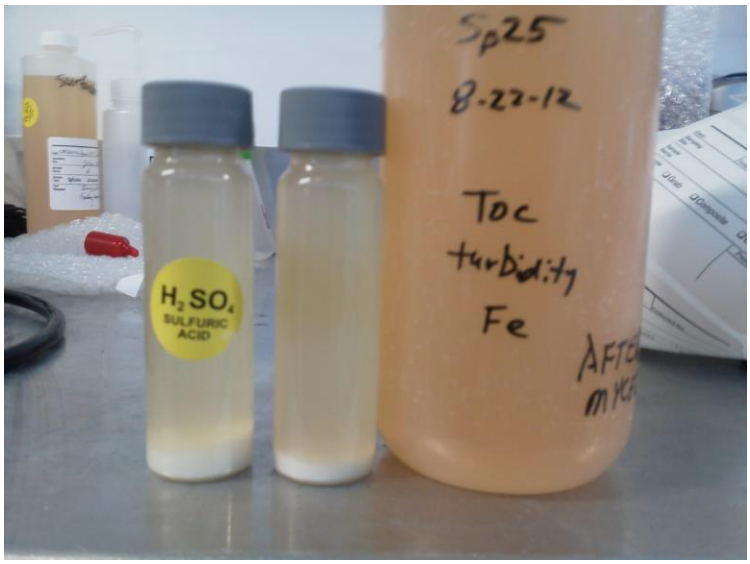


Figure 4. Photo of source water in holding pond, prior to transfer to holding tank and treatment unit. Ponds are aerated with bubblers. Oxidized iron staining in water clearly visible.

Appendix C

Reference

1. Altare, C.R., et al., *Regeneration and long-term stability of surfactant-modified zeolite for removal of volatile organic compounds from produced water.* Microporous and Mesoporous Materials, 2007. **105**(3): p. 305-316.

Appendix C

Addendum 1. SEM/EDAX results from H_2SO_4-acidified precipitate, 1 and 20 µm filter sizes.