Water Quality Required for Fracturing Gas Shales: Cost Effective Analytic and Treatment Technology

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ABSTRACT

Shale gas development relies heavily on multi-stage hydraulic fracturing (HF) to maximize the economic viability of each new well. Industry is making a concerted effort both to recycle and re-use produced brine from fracturing operations and to use alternate water sources for well operations. Some experts foresee almost all produced brines being treated and reused within the next five years. Texas A&M Global Petroleum Research Institute (GPRI) has been one of the leaders in promoting new technology to reach these goals. In the past decade we have conducted a number of field trials in different shale plays to a) identify technologies and determine their effectiveness, b) field test advanced monitoring and measurement techniques, and c) integrate the technologies into one cost-effective program for the O&G industry.

This paper presents results from these trials that compare different types of filtration media used to remove hydrocarbons, filtration techniques to remove suspended solids and nano filtration materials to stabilize ultra-high salinity brines making them compatible with today’s fracturing fluid designs. In addition to describing cost effective brine treatment, we have provided a venue for testing advanced analytical techniques that provide rapid ways to measure the effectiveness of such water treatment. Measuring hydrocarbon content in the brines aids in selection of optimal treatment and monitoring of its effectiveness. New fluid imaging techniques characterize particulates in brines and can help to optimize filtration requirements. Biological monitoring can determine effectiveness of solids removal practices and helps in selection of appropriate bacterial control.

The paper will discuss the need to utilize on-site, real-time analysis of produced water and frac flow back brine to allow faster and more accurate characterization of the oil and gas waters being cycled back to unconventional gas development.

The benefits of the technology come from improved procedures to characterize and mitigate the risks of HF at drilling and hydraulic fracturing sites. Better monitoring and treatment can help to counter the mounting concerns of legislators, regulatory agencies, and the general public as well as aid the economic development of our natural gas resources.
INTRODUCTION

Impact of Multi-stage Hydraulic Fracturing of Shale; Technical & Environmental

The technical advances that have brought about the shale production revolution are well known. Impacts, economically and socially are profound. However the environmental “footprint” of shale development is much larger than development of conventional resources. The industry now needs significant technical advances in operational practices in order to reduce the environmental impact of these abundant unconventional resources. One of the greatest needs our industry has at present is to address both the technical and environmental issues of produced water management.

Water Quality Requirements for Fracturing Fluids

Production engineers responsible for shale gas operations are discovering that produced water management has become almost as important as handling gas and oil. With recent well HF operations requiring upwards of 10 million gallons of water for fracturing, the acquisition, transportation, storage, treatment, and disposal can represent not only a significant percentage of total well costs, but may also add weeks or months to well construction. In recent years arguments for and against the use of fresh water sources (surface and subsurface aquifers) have confounded the problem. Contributing to the uncertainty is the fact that no set water quality standards have been established for fracturing –even quality guidelines can be misleading. Fortunately the industry consensus is becoming clearer that fresh water is not necessary for fracturing operations and the produced water from fracturing operations can be reused if proper treatment is performed before recycling. Frac water quality will be dependent on frac fluid design but new chemicals and new practices allow latitude in water type. Water quality standards still should be established however and information addressing how to meet these standards is equally important.

This paper aims to set a standard water quality for brines destined for re-use as frac fluids. It also describes what a 4 year program of both pilot plant and field trials have found to be effective treatment methods for achieving that water quality. And along the way we discuss better on-site analytical methodology that can be used to measure those water quality standards.

Public Perception Will Impact Decisions on Water Management

Public perception matters. Regulatory practices are developed based on the need to protect public water resources. Reaching a consensus on water quality requirements would not only benefit industry but would help to alleviate public concerns about fracturing. Objections to fracturing can be reduced by changes in oil field practices such as using brackish ground water and re-using produced brine. In certain South Texas counties, fresh water use for drilling and HF operations is as great as municipal utilization (Griffin, 2013)\(^1\). Community concerns are common. Water districts are proliferating in O&G operating areas and obtaining approvals for fresh water wells will become more difficult and time consuming even if landowners are willing to sell their rights. In December 2013, the Texas Water Development Board’s monitoring well in La Salle County showed water in the Carrizo-Wilcox aquifer at 496 feet below the surface, a drop of 247 feet from where it was 10 years ago (Hiller 2013)\(^2\). It is clear that the use of alternate water resources for fracturing would represent a tremendous plus for the industry and would help a great deal with public perception (Theodori, 2013)\(^3\).

\(^{1}\) Griffin, J. M., Mosbacher Institute http://bush.tamu.edu/mosbacher/program/ege/
\(^{2}\) Hiller, J. “Oil & Gas Boom Requiring More Water Than We Have”, San Antonio Express News, December 14, 2013
\(^{3}\) Theodori, G. Perception of the Natural Gas Industry and Engagement in Individual Civic Actions, Journal of Rural Social Sciences, 28(2), 2013, pp. 122–134
FRAC WATER QUALITY REQUIREMENTS

As operators turn to brackish water, produced water from previously fractured wells, or even municipal waste water, the water treatment service industry has adapted in order to provide the services necessary to manage the resource. Attendant with this growth, the need for fracturing water quality standards becomes more important. Understanding the complexity of frac fluid design, it will be difficult to reach consensus on standards. Nevertheless industry experience from 40 years’ experience in water flooding (Craig 1971, Wilhite 1986, Rose et al 1989) can be used as a starting point. Whatever the types of treatment being used to treat waters for re-use, the removal of three major types of material is a priority.

- Removal of residual hydrocarbon and oleophilic materials
- Removal of suspended solids
- Partial removal of soluble minerals and metals to make solutions thermodynamically stable at ambient conditions in oxygenated systems.

Water treatment systems should be robust as well. Emulsions containing suspended solids and hydrocarbon often are the downfall of produced water treatment processes. Process trains must guard against system upsets and occurrence of flowback of frac chemicals in produced brines. Later in this paper we show an example of field brine containing enough slop to shut down a water treatment facility if not removed. Suspended solids tend to plug filtration media and foul membranes just as such substances causes formation damage in injection wells and poorly drilled producing wells in conventional plays (Mitchell 1981, Ahmadun 2009). (Interested researchers can find references to George Maly’s work at Union Oil Company dating back to the 1950s).

Technologies used to remove suspended solids in produced water should effectively reduce biological activity. Micro and ultra-filtration membrane filters have become a popular treatment option to remove bacteria thereby reducing biocides requirements and helping in the avoidance of microbial contamination of formations.

Finally, because produced waters are often thermodynamically unstable in oxygenated brines, it becomes necessary to remove partially soluble products such as iron oxide and other scaling compounds. Selective removal of such ionic species can be performed by either chemical flocculation/precipitation or by use of nanofiltration membranes that reduce such specifics.

PRODUCED WATER TREATMENT TECHNOLOGIES

There are a number of technologies developed for produced water treatment. Recent reviews include comprehensive lists of the possible options for treatment. These reviews provide a good fundamental knowledge of the technology but fall short when an operator must decide which processes are considered technologically advanced enough for field operations and whether they are ready for produced water management in oil field operations. The problem lies in the selection of an appropriate technology for a particular application. While most operators seek companies who have field experience and a track record of commercial operations, the field is limited and new companies with new technology may offer cost or scheduling advantages for planned projects. The objective of the GPRI A&M team through its Technology Integration Program (TIP) has been to provide a means whereby companies can get access to field trials of new technologies. It is expected that

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the EFD-TIP will be identifying and facilitating the integration of various projects/programs that can impact the unconventional natural gas developments in an environmentally sensitive and cost effective manner.

**PRE-TREATMENT CONCEPTS**

This report and other technical papers refer to “pretreatment” when it comes to produced water processes. The term is a colloquialism that represents the types of treatment performed on brines before the main process is employed to clean brines. Essentially all produced water treatment technology whether it is thermal desalination, electrocoagulation, or membrane filtration benefits from pretreatment to remove troublesome materials from the waste stream before treatment. Pre-treatment includes cartridge filters for removal of large particulates, media filters (sand filters et al.) and specially designed media for hydrocarbon removal. Pretreatment also includes what is commonly referred to as “floc and drop” technology that utilizes chemical flocculants and filter techniques to remove contaminants. Dissolve air flotation is considered a pretreatment as well as micro and ultra-membrane filtration technique. All of the pretreatment techniques provide low cost removal of contaminants – the problem is deciding how much of the material left is still capable of damaging a well or reducing the treatment efficiency of the main treatment process.

**THIS TECHNICAL PAPER CONCENTRATES ON A&M'S EVALUATION OF VARIOUS PRE-TREATMENT TECHNOLOGIES SUITABLE FOR FIELD COMMERCIALIZATION. WATER (PRE) TREATMENT PROCESSES**

As mentioned there is ample literature on the types of technology that could be used for produced water treatment (SPE 2013, RPSEA 2009)\(^\text{13,14}\). The Colorado School of Mines\(^\text{15}\) assessed 54 types of technologies over a two year period and reported in 2011. Their review classified systems into stand-alone technologies or combined treatment processes while our team’s approach has been to actually try to evaluate as many of the processes as possible in field trials.

Research on water treatment technologies must invariably turn to actual use of field brines to accurately represent conditions encountered by a treatment system. Additionally while most water treatment techniques function adequately in low salinity waters, the ultra-high salinity of the oil field stymie many otherwise practical techniques perfected for fresh water systems. Finally to determine if a technology is “field ready”, practitioners must perform extended duration testing to measure the robustness of the process being evaluated. Most of these operating parameters cannot be met in a laboratory environment and are seldom achieved in pilot plant operations. For these reasons, our research turned to extended duration tests conducted from to 6 weeks duration. Field trials also concentrated mostly on pre-treatment technology as the preferred method to manage the wide range of ultra-high salinity systems encountered.

Figure 1 shows a graphic of the various field trials conducted by the team over a three year period. Trials were conducted in the Marcellus Shale (3 trials), Eagle Ford Shale (3 trials), Barnett Shale (2 trials), Woodford Shale (3 trials), and the Permian Basin (1 trial). Testing was standardized and several technologies were evaluated at a particular site. Analytical tests were performed on site with various technologies and baseline sample analyses were carried out by certified environmental laboratories.

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\(^{14}\) Technical Assessment of Produced Water Treatment Technologies, RPSEA Project 07122-12 Colorado School of Mines November, 2009

\(^{15}\) Xu, Pei, Tzahi, C., Drewes, J. E., Novel and Emerging Technologies for Produced Water Treatment, Colorado School of Mines, EPA Technical Workshop for Hydraulic Fracturing, March 2011
Figure 1. Experiences in multiple field trials in multiple shale plays provide good examples of how produced water technologies compare.

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. Analytical monitoring of brines on-site was compared to laboratory analyses of the same samples to validate techniques. Figure 2 shows the general measurements that made up the analytical monitoring program.

**Membrane Pretreatment Process Train Designs**

Work at A&M began on produced water treatment in early 2000 (Siddiqui 2002). Laboratory and pilot plant testing have been reported in a number of publications. A process train for field operations in the Marcellus Shale

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was designed and tested in pilot plant studies beginning in 2009\textsuperscript{17}. The basic design was chosen to be adaptable to specific field conditions and subsequently has been found to be satisfactory in all shale plays to date. Not including analyte design, there are three main components to our concept of pre-treatment used in this report, hydrocarbon removal, suspended solids removal, and dissolved solids (partial) removal. In all cases, these basic procedures were sufficient to produce brines that would meet anyone’s specifications for an effective fracturing fluid.

**Technology for Removal of Hydrocarbons,**

One of the basic tenets of water conditioning for water flooding in conventional reservoirs such as Alaska’s Prudhoe Bay and West Texas’ Permian Basin operations is thorough hydrocarbon removal. Many of the unconventional gas shale plays are dry gas production such as the Marcellus Shale so that traditional production batteries weren’t expected to handle large amounts of liquid crude oil. However as operators began to drill and produce liquid hydrocarbons from the shales (Eagle Ford, Bakken, Woodford), produced water containing hydrocarbons became common. Hydrocarbons not only aggravate fouling, they also provide nourishment for bacterial growth. Additionally the large multi-stage frac fluid volumes tended to have frac chemicals in early stage flowback, often emulsified. Essentially all water treatment systems experience upsets when hit with these types of hydrocarbons. The GPRI mobile lab experienced this during a trial testing salt water treatment alongside a disposal well in the Permian Basin Figure 3 shows a cartridge guard filter used in a the trial in the Permian Basin when a slug of slop came through the brine gathering system to the salt water disposal well. All field trials planned in the future will have robust hydrocarbon and emulsion removal as pretreatment.

**Suspended Solids Removal**

Figure 3 shows a cartridge guard filter that intercepted slop carryover from the SWD line coming from field brine gathering system. This slop is emulsified polymer, oil and suspended solids (commonly referred to as “schmoo"
Microfiltration and ultrafiltration technology has undergone rapid advancement in the past decade. Work in the late 1990s and early 2000s focused on membrane filtration utilizing “loose” reverse osmosis membranes and the majority of commercial filtration operations utilized spiral wrapped polymer membranes to remove total suspended solids (TSS). Early field trials to treat oil field brines by Frankiewicz 18 found spiral wrapped membrane systems were prone to fouling. Pilot plant and early field trials in the Barnett Shale also showed that microfilters were effective in removing suspended solids included bacteria but suffered from premature fouling.

As technology progressed for municipal water treatment, microfilters with different designs were introduced. The A&M program evaluated a large number of filters. Experience gained during a number of field trials led to the adoption of micro-filtration processes that included mechanical cleaning. All new TSS removal technology in our future trials will include such efficient TSS removal (or a cost effective equivalent).

**Dissolved Metals and Scaling Ions Removal**

If produced water is to be re-used in fracturing operations, operators normally use makeup water to achieve the necessary volume for treatment. Produced brine dilution minimizes total ionic strength of the final use fluid and simplifies treatment options that can be employed. A&M uses nanofiltration for selective removal.

Spiral wrapped membrane filtration using “loose reverse osmosis” membranes has gained favor in the industry for a number of beneficial reasons. Nanofiltration membranes can be selected to reject certain dissolved ions while leaving other materials in the brines. Selective ion removal allows operators to remove such troublesome materials as sulfates (incompatibility issues with seawater), partially soluble species such as iron, and certain metal materials that interfere with frac fluid packages. This selective removal leaving behind benign material affords membranes a strategic advantage over distillation techniques.

The lower pressure required to selectively remove materials results in better performance than reverse osmosis membranes Higher salinity brines can be processed with ease. Process trains operate with lower volumes of rejected fluids that require disposal. Finally such process trains experience longer functional lives for the filters.

**FIELD OPERATIONS TO VALIDATE TREATMENT PROCESSES**

Validating new technology under field-operating conditions is imperative. Field ops allow gathering of performance data on process systems so that engineering can scale up such systems to full-size commercial operations. With the financial assistance from both industry and the government, the GPRI team was able to design and construct a field mobile laboratory/treatment trailer. The mobile unit incorporated the equipment necessary to test various technologies in a continuous process train and to monitor performance with on-site testing. Figure 4 shows the unit in South Texas in the summer of 2013.

ANALYTICAL TESTING DURING FIELD TRIALS

Water Quality Measurement--- why do we care? My colleague at the Houston Advanced Research Center often says “What can be measured, can be changed”. This tenet guides our field research program to a great degree. Technology advances have brought significantly superior processes to produced water management. Nevertheless it is imperative to know quantitatively the characteristics of the brines so that a) standard brine specifications can be monitored and met and b) to have information that can be used to identify “what went wrong” when systems fail to meet expectations. The work in our programs depends to a great degree on finding and utilizing the best and most cost effective analytical technology that will work in field operations.¹⁹

**Advanced Analytical Technology**

An industry/government collaboration was created to fund the evaluation of advanced analytical technology suitable for monitoring our efforts in the TIP effort²⁰. The EFD team conducted multiple field trials in 2011, 2012, 2013, and 2014 representing more than 6 months in the field conducting trials. Tests were performed in the Permian Basin, Eagle Ford Shale, Woodford Shale, and the Eaglebine. At each location the team used specially developed analytical technology to allow on-site and real-time measurement of process train performance. We also collected samples to send to certified environmental laboratories to provide a baseline reference for on-site testing.

Figure 2 (page 8 of this paper) previously showed what we typically test in the field. For hydrocarbon removal, a total organic carbon (TOC) analyzer proved to be the most effective monitor²¹. The device allows direct measurement of organic material in ultra-high saline waters without having any dilution of filtration. Efficiency of

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¹⁹ [https://sites.google.com/site/amadvancedanalytics/](https://sites.google.com/site/amadvancedanalytics/)


²¹ [www.geinstruments.com/](http://www.geinstruments.com/)
hydrocarbon removal was determined by measuring both before and after samples from the process train. Figure 5 shows the unit in the field lab being used to provide TOC analysis of samples from an oil coalescing unit installed at a trial in Pennsylvania.\(^2\)

![Figure 5. Total Organic Carbon analyzer in a field setting.](Image)

The analyzer samples do not require any preparation or dilution prior to analysis. Ultra-high salinity brines do not interfere with or degrade results from the instrument.

At one site, a modified zeolite media was used to remove BETX. To measure the removal of these volatile solvents, a specialized BETX analyzer\(^2\) unit was tested on site to measure brine samples taken directly from the process train. (Figure 6 shows the unit in operation.) While the team site was quite satisfied with the unit, the cost of the instrument made its inclusion too expensive to include in analytical testing in subsequent trials.

![Figure 6. The BETX analyzer was developed to measure volatile aromatics at DoD sites undergoing remediation. The analyzer was able to detect BETX in produced water at ppb concentrations.](Image)

Field kits from two manufacturers were evaluated in our trials. These kits provided a number of chemistries to measure the content of ionic species in the brines. The technology has been based on extensive work in fresh water environmental monitoring but modified to handling the high ionic strength solutions. Figure 7 shows one of the kits being used in the mobile lab to measure dissolved iron removal by microfiltration\(^2\). While some accuracy is lost, the technologies have been adequate to detect differences in “upstream” and “downstream” samples.

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\(^2\) [https://sites.google.com/site/amgprribgexcogroupfieldtrial/performance-of-system/media-filtration--oil-removal/cetco-oil-coalescer-system](https://sites.google.com/site/amgprribgexcogroupfieldtrial/performance-of-system/media-filtration--oil-removal/cetco-oil-coalescer-system)


\(^2\) [www.hach.com/bart-test-combination-package](www.hach.com/bart-test-combination-package)
Figure 7 shows the dissolved ion instrument utilized for field measurement of brine composition. Analyses typically include chlorides, sulfate, and carbonate anionic species and calcium, boron, and iron cationic analytes.

Monitoring of biological activity has become more important as the volume of produced water being recycled grows. One of our team’s priorities for 2015 and beyond is to identify cost affordable biological monitoring on-site and under real-time conditions. Currently samples are taken before and after each step of the process train for monitoring. Specially formulated media promotes growth.

Currently Hach vials are the handiest method for identifying the presence of bacteria. Figure 8 shows a set of five vials, each with a special mix of growth media to promote activity. The concentration of the bacteria is estimated by the growth of the biological agent over a several day period. At the 2014 trial, technicians collected samples on the raw water on the first day of the trials – Table 1 shows the results after 4 days. The field samples were clearly contaminated.

Table 1. Incubation of field Samples to Determine Biological Activity

<table>
<thead>
<tr>
<th>Feed Sample</th>
<th>Incubation Dates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacteria Tested For</td>
<td>10/1/2014</td>
</tr>
<tr>
<td>Sulfate Reducing</td>
<td>No</td>
</tr>
<tr>
<td>Slime Forming</td>
<td>Yes</td>
</tr>
<tr>
<td>Heterotrophic Aerobic</td>
<td>Yes</td>
</tr>
<tr>
<td>Acid Producing</td>
<td>No</td>
</tr>
<tr>
<td>Iron Reducing</td>
<td>Yes</td>
</tr>
</tbody>
</table>

RESULTS OF WATER TREATMENT TRIALS

Oils and Emulsions Removal

As operators have begun to develop the shales that contained liquid hydrocarbons (Eagle Ford, Bakken, Woodford), produced water containing hydrocarbons are more common. The large gelled-polymer multi-stage
frac fluid volumes tended to have frac chemicals in early stage flowback, often emulsified. Essentially all water
treatment systems experience upsets when hit with these types of slugs. For this reason all process trains used in
GPRI field trials used some form of guard filters for emulsified oils. The GPRI mobile lab experienced this during a
trial testing salt water treatment alongside a disposal well in the Permian Basin (refer to Figure 3) when a slug
came through the brine gathering system to the salt water disposal well.

Several hydrocarbon removal systems were tested in the process train in the mobile laboratory. A number of
systems were tested that were designed to remove BETX from the brine including a modified zeolite catalyst from
Los Alamos National Laboratory (Sullivan et al)\textsuperscript{25}. Other media tested have included synthetic adsorbents\textsuperscript{26, 27}. One of the more successful filter guards used an oil coalescing process to minimize pass through of
hydrocarbons\textsuperscript{28}.

**Suspended Solids Removal (Microfiltration)**

Early on, it became clear that rigorous solids removal from brine streams would be necessary if the brines were to
be re-used. Technologies adopted from municipal waste water treatments such as flocculation of contaminants,
precipitation, and filtration were adopted by early water service providers. Unfortunately these practices use
large quantities of chemicals and produce large volumes of waste because of the ultra-high solids loading of
produced water. A much less costly and more efficient method is to use crossflow microfiltration to remove solid
contaminants.

Crossflow filtration is just one of the important advances in microfiltration and ultrafiltration technology in the
last decade. With the boom in gas shale development, there are numerous new designs, new materials, and new
processes to resist fouling (Burnett)\textsuperscript{29}. The introduction of hollow fiber ultra-filters into the municipal water
treatment market opened the door for O&G application where high solids loading were common in high salinity
brines.

Microfiltration offers the most cost effective way to remove solids from turbid systems. Figure 9a and 9b show
suspended solids removal from a field sample. These filters typically run at pressures from 30 to 50 psi and can
provide up to 80% separation efficiency in a recycle mode. Power cost to run these filters, measured during the
A&M trials showed average microfiltration power costs of less than $0.006 per barrel.

![Figure 9A. Micro-Filter Performance. Photo 3 shows a sample collected during the microfilter run mid-test.](image)

![Figure 9B. Turbidity tracks suspended solids and hydrocarbon content. Micro-filtration effectively removes the contaminants that would cause formation damage.](image)


\textsuperscript{26} http://www.mycelx.com

\textsuperscript{27} http://www.polymerventures.com

\textsuperscript{28} www.CETCO.com

\textsuperscript{29} Burnett, D. B. “Recovery of Fresh Water Resources from Desalination of Brine Produced during Oil and Gas Production Operations,” Report, Texas Water Development Board, Sept., 2004
In early field trials conducted in the Marcellus Shale, micro filters tended to foul after extended use. The use of spiral wound polymeric filters was halted and testing began with specially made hollow fiber filters and hollow tube filters. Figure 10 shows that hollow fiber microfiltration was acceptable but at the expense of fairly low permeate flow rates. Later testing employed 12 ft. long modules that provided greater filtration surfaces. These latter devices also were configured to allow mechanical cleaning, a marked improvement in flow performance.

![Experimental Ultra-Filter Produced Brine](image)

Figure 10. The chart shows permeate rate as a function of time and total throughput. The decreasing slope of the line indicates gradual loss in flow during the duration of the test.

The efficiency and long term flow performance of the micro filters has improved with the advent of microfiltration using mechanical cleaning techniques. Service sector operators may now choose between different types of cleaning and different types of microfiltration. Hollow tube filters can be cleaned by pumping sponge balls through the filter in the same manner as pipeline pigs. Both this type and a ceramic filter (shown in Figure 11) were evaluated in West Texas.

![Hollow Tube Filters](image)

![Ceramic Filters](image)

Figure 11 shows both types of microfiltration modules. The horizontal filter module contains polymeric hollow tube filters while the upright module contains ceramic filters. Each filter, in turn was tested in the process train, preceded by hydrocarbon removal. Output from the filters were directed to the nan filter for dissolved solids removal.

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Figure 12 shows performance of a mechanically cleaned hollow tube micro filter that was employed in West Texas. The momentary drops in flow rate represent the times when the cleaning balls were pumped through the system.

![Hollow Tube Permeate Rates](image)

Figure 12 shows permeate flow rate vs. cumulative volume produced during a trial run. The breaks in the chart line represent pressure changes associated with sponge ball passage through the system.

Ceramic micro filters are becoming an alternate option for pretreatment. This equipment was used most recently. Figure 13 shows the trial employing microfiltration with a system that utilized automated back pulsing and backwashing at regular intervals.

![Microfiltration Permeate Flow](image)

Both types of filters were tested under the same conditions so that an easier comparison could be made of their filtration efficiency. The hollow tube filter shown in Figure 12 was housed in a 12 ft. long module and had 18, ½” tubes with 28 ft² (2.6 m²) of surface area. The actively cleaned ceramic filters contained in a 4’ housing with 3 membranes with a total of (0.68 m²) of surface area provided higher flux. Comparing the performance of the filters as shown in the charts shows that the ceramic filters gave more than 5 times greater flow efficiency under the same operating conditions. Both filters provided superior quality permeates with NTU
turbidities less than 2.0.

**Dissolved Solids Removal (Nanofiltration)**

*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 2 shows the inlet and outlet iron content measured on-site in Washington Co.

Table 2 Nano-Filtration Ultra-High Salinity Brine

<table>
<thead>
<tr>
<th>sample #</th>
<th>tds</th>
<th>turbidity</th>
<th>conductivit</th>
<th>toc</th>
<th>iron</th>
<th>pH</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN 6</td>
<td>184.2</td>
<td>0.68</td>
<td>111.1</td>
<td></td>
<td>9.7</td>
<td>6.16</td>
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</tr>
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<td>SN 7</td>
<td>184.5</td>
<td>0.79</td>
<td>111.6</td>
<td></td>
<td>9.7</td>
<td>6.16</td>
<td>Nano permeate</td>
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<td>SN 8</td>
<td>195</td>
<td>0.9</td>
<td>120.2</td>
<td>113</td>
<td>10.2</td>
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<td>0.4</td>
<td>114.7</td>
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<td>12.6</td>
<td>6.1</td>
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<td>SN 10</td>
<td>200.7</td>
<td>0.8</td>
<td>121.2</td>
<td>120</td>
<td>11.9</td>
<td>6.11</td>
<td>Nano Feed</td>
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<td>SN 11</td>
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<td>0.5</td>
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<td>75.3</td>
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<td>6.11</td>
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<td>SN 12A &amp;</td>
<td>202</td>
<td>0.67</td>
<td>127.3</td>
<td>167</td>
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<td>121.5</td>
<td>94.4</td>
<td>11.4</td>
<td>6.19</td>
<td>Nano Feed split smple</td>
</tr>
</tbody>
</table>

A second indicator of nano-filtration performance efficiency is the filtration efficiency of the component. Figure 14 shows the pressure-rate data of a nano-filtration run with brine that had been pre-treated with micro-filtration.

![Figure 14. Nanofiltration Data from 2014 test in the Permian Basin. The filter is a Dow nanofilter designed specifically for rejection of sulfates from seawater.](image)

**Performance Comparisons of Treatment Technologies**

Over the period 2011 through 2014 over 20 field trials were performed, each testing multiple water treatment technologies and advanced analytic monitoring. Each of the trials was preceded by extended trials that were carried out in the A&M pilot plant facilities for produced water treatment. Produced water, trucked to the facility allowed the team to run tests at near real life field operating conditions. Technologies deemed successful or qualified successes were scheduled for subsequent extended duration field trials. This evaluation procedure
allowed our team to compare performance of technologies, both isolated and in a process train where each technology had to perform effectively to allow the next step in the process to operate in its designed manner.

Results show that hydrocarbon removal prior to any filtration testing is a safe decision. Treatment adds little to the overall cost of operations and serves to guard against system upsets. Choices between hydrocarbon removal by media or by cartridge filtration vs. oil coalescers depended upon the oil content of the raw feed water. Both options reduced hydrocarbon content satisfactorily. Field engineers tended to prefer the coalescer systems because the vendor provided field ready systems that required little attention in operations.

Side by side field trial comparisons of microfiltration performance showed the superiority of this technology to the more cumbersome and costly flocculation, precipitation, and filtration to remove suspended solids from the brines. Such pretreatment is appropriate for essentially all water treatment technologies used in the industry.

Brine softening by nanofiltration was found to be an effective way to create clean “10 lb. brines” that have been proven base fluids for recycled fracturing brines. New designs of nanofiltration operate at significantly lower pressures than that of their predecessors and thus afford lower operating costs to the operator.

Comparison of Costs; Operating Cost of the Process Train

In the field trial in Midland Texas, the team processed more than 10,000 gallons of brine at an average power cost of $0.26 per bbl. Table 3 shows a breakdown of power costs for each flow loop with hydrocarbon removal requiring $.0006 per barrel of fluid treated, suspended solids removal power costs of $.06 per barrel of fluid, and suspended solids partial removal (brine softening) of $.09 per barrel of brine processed. Total power costs including backwashing and repressurization came to a total of $.26 per barrel of clean brine produced.

To estimate total operating costs, produced water treatment systems can be compared to seawater desalination processes. In commercial desalination power costs represent from 15% to 25% of total operating costs depending on design of energy recovery techniques. The use of microfiltration and nanofiltration for produced water systems are therefore approximately $1.50 per bbl. Since published costs for more traditional produced water treatments can be as much as $6.00 per bbl., the use of membrane pretreatment becomes a logical choice for future facilities.

Table 3 shows actual operating data for a daily run of the A&M mobile facility. Numbers are taken from the variable frequency drive (VFD) controllers of the process train pumping.

<table>
<thead>
<tr>
<th>Date of Run</th>
<th>Pretreatment flow loop</th>
<th>Microfiltration flow loop</th>
<th>Nanofiltration flow loop</th>
<th>total power</th>
</tr>
</thead>
<tbody>
<tr>
<td>30-Sep</td>
<td>19.4</td>
<td>218.9</td>
<td>51.3</td>
<td></td>
</tr>
<tr>
<td>1-Oct</td>
<td>19.4</td>
<td>218.9</td>
<td>51.3</td>
<td></td>
</tr>
<tr>
<td>2-Oct</td>
<td>20.9</td>
<td>230.6</td>
<td>57.9</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>power used each unit</th>
<th>1.5</th>
<th>11.7</th>
<th>6.6</th>
<th>19.8 kwh</th>
<th>total power</th>
</tr>
</thead>
<tbody>
<tr>
<td>value of power</td>
<td>0.195</td>
<td>1.521</td>
<td>0.858</td>
<td>2.574 $ @ 0.13/kwr</td>
<td></td>
</tr>
<tr>
<td>volumes</td>
<td>1271.46</td>
<td>1007.35</td>
<td>380.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>volume oil field units</td>
<td>30.27285714</td>
<td>23.984524</td>
<td>9.0547619</td>
<td>bbls</td>
<td></td>
</tr>
</tbody>
</table>

| cost to treat | 0.006441414 | 0.0634159 | 0.09475677 | 0.28427 $/bbl final cost | Pumping Cost |
CONCLUSIONS AND RECOMMENDATIONS

Extensive testing of water treatment technologies under field conditions have proven that new membrane pre-treatment processes are a robust and cost effective alternative to traditional processes for produced water treatment. Such technologies lower capital costs, reduce chemical costs, simplify field operations and provide an environmentally friendlier way to recycle brines for re-use. Additionally the trials, conducted in a number of shale basins showed that the same basic treatment technology is appropriate for a wide range of field conditions and brine water compositions.

On-site analytical monitoring is recommended for all instances where produced water is treated for reuse, not only to determine the effectiveness of treatment but also to reduce the cost of environmental laboratory analysis and to provide information for regulatory requirements.

FUTURE WORK (2015 -2016)

Work is continuing on both the Technology Integration Program effort and the Advanced Analytics program. Efforts are planned to evaluate more advanced biological activity monitoring and design is underway to incorporate more in-line analytical monitoring for the process train.

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REFERENCES

References are placed on the appropriate page of the paper.