

# **Cost Effective Recovery of Low-TDS Frac Flowback Water for Re-use**

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**Harish R. Acharya**

Principal Investigator  
518-387-5875 (Telephone)  
518-387-7403 (Fax)

**Claire Henderson  
Hope Matis  
Hareesh Kommepalli  
Brian Moore  
Hua Wang**

**GE Global Research**  
1 Research Circle, Niskayuna, NY 12309-1027

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## **ABSTRACT**

The project goal was to develop a cost-effective water recovery process to reduce the costs and environmental impact of shale gas production. This effort sought to develop both a flowback water pretreatment process and a membrane-based partial demineralization process for the treatment of the low-Total Dissolved Solids (TDS) portion of the flowback water produced during hydrofracturing operations. The TDS cutoff for consideration in this project is < 35,000 ~ 45,000 ppm, which is the typical limit for economic water recovery employing reverse osmosis (RO) type membrane desalination processes. The ultimate objective is the production of clean, reclaimed water suitable for re-use in hydrofracturing operations.

The team successfully compiled data on flowback composition and other attributes across multiple shale plays, identified the likely applicability of membrane treatment processes in those shales, and expanded the proposed product portfolio to include four options suitable for various reuse or discharge applications. Pretreatment technologies were evaluated at the lab scale and down-selected based upon their efficacy in removing key contaminants. The chosen technologies were further validated by performing membrane fouling studies with treated flowback water to demonstrate the technical feasibility of flowback treatment with RO membranes. Process flow schemes were constructed for each of the four product options based on experimental performance data from actual flowback water treatment studies. For the products requiring membrane treatment, membrane system modeling software was used to create designs for enhanced water recovery beyond the typical seawater desalination benchmark. System costs based upon vendor and internal cost information for all process flow schemes were generated and are below target and in line with customer expectations. Finally, to account for temporal and geographic variability in flowback characteristics as well as local disposal costs and regulations, a parametric value assessment tool was created to assess the economic attractiveness of a given flowback recovery process relative to conventional disposal for any combination of anticipated flowback TDS and local disposal cost. It is concluded that membrane systems in combination with appropriate pretreatment technologies can provide cost-effective recovery of low-TDS flowback water for either beneficial reuse or safe surface discharge.

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## List of Acronyms

<b>Acronym</b>	<b>Definition</b>
bbbl	Barrel (1 bbl = 42 gallons)
Conventional	Conventional Flowback Water Disposal Process based on Class II SWD
$C_{\text{Chemicals}}$	Cost of process chemicals, \$/bbl flowback
$C_{\text{Conventional}}$	Cost of Conventional Flowback Water Disposal Process, \$
$C_{\text{Disposal}}$	Cost of flowback disposal ( $= C_{\text{Transport}} + C_{\text{SWD}}$ ), \$/bbl
$C_{\text{FWRP}}$	Cost of Flowback Water Recovery Process, \$
$C_{\text{Fresh Water}}$	Cost of fresh water for frac use, \$/bbl
$C_{\text{Maintenance}}$	Cost of annual maintenance per annual feed processed, \$/bbl flowback
$C_{\text{Penalty\_Avoid}}$	Value of penalty avoided due to flowback re-use
$C_{\text{Process}}$	Cost of process steps (capital and operating expenses), \$/bbl feed
$C_{\text{Product Delivery}}$	Cost of product delivery to re-use site, \$/bbl product
$C_{\text{Product\_Value}}$	Value of fresh water avoided due to flowback re-use, \$/bbl product
$C_{\text{Recovery}}$	Cost of product recovery ( $= C_{\text{Treatment}} + C_{\text{Product Delivery}} - C_{\text{Product\_Value}} + C_{\text{Penalty\_Avoid}}$ ), \$/bbl product
$C_{\text{SWD}}$	Cost of saline water disposal by deep well injection, \$/bbl
$C_{\text{Setup}}$	Cost of mobile rig transportation and setup at the frac site, \$/bbl feed
$C_{\text{Treatment}}$	Cost of flowback treatment to produce product ( $= C_{\text{Setup}} + C_{\text{Process}}$ ), \$/bbl feed
$C_{\text{Transport}}$	Cost of transportation of disposal water, \$/bbl flowback or concentrate
$C_{\text{Waste}}$	Cost of FWRP process waste disposal, \$/bbl flowback
"Cut-off" TDS	The value of $y_F$ where the $C_{\text{FWRP}}/C_{\text{Conventional}} = 1$ represents the economical "cut-off" TDS for that particular frac flowback site.
F	Flowback volume, bbls
FWRP	Flowback Water Recovery Process
GE	General Electric
GEGR	General Electric Global Research
GEW&PT	General Electric Water & Process Technologies
MF	Microfiltration
MMcf	Million cubic feet
NF	Nanofiltration
NTU	Turbidity measurement unit
RO	Reverse Osmosis
SWD	Saline water disposal – deep injection Class II well
SRB	Sulfate reducing bacteria
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
UF	Ultrafiltration
X	Extent of flowback recovered, bbl product/bbl flowback
$X_{\text{Pretreatment}}$	Extent of flowback recovered after pretreatment prior to membrane desalination), bbl/bbl flowback
$y_F$	Feed TDS concentration, ppm
$y_{\text{Concentrate}}$	Concentrate (sent to SWD) TDS concentration, ppm
$y_{\text{Distillate}}$	Distillate (from thermal evaporator) TDS concentration, ppm
$y_{\text{Permeate}}$	Permeate (from membrane) TDS concentration, ppm
$y_{\text{Product}}$	Product TDS concentration, ppm
$y_{\text{Retentate}}$	Membrane retentate (reject) TDS concentration, ppm

## EXECUTIVE SUMMARY

This is the final report for this project supported by U.S. DOE NETL (Contract No. DE-FE0000784) and GE Global Research (GEGR). This report provides a project narrative and a summary of project activities and accomplishments for the reporting period, beginning October 1, 2009 and ending March 30, 2011.

The project goal was to develop a cost-effective water recovery process to reduce the costs and environmental impact of shale gas production. This effort sought to develop both a flowback water pre-treatment process and a membrane-based partial demineralization process for the treatment of the low-Total Dissolved Solids (TDS) portion of the flowback water produced during hydrofracturing operations. The TDS cutoff for consideration in this project is < 35,000 ~ 45,000 ppm, which is the typical limit for economic water recovery employing reverse osmosis (RO) type membrane desalination processes. The ultimate objective is the production of clean, reclaimed water suitable for re-use in hydrofracturing operations.

Over the past year, the shale gas industry appears to be continuously evolving in terms of methodologies and technologies used for hydrofracturing. Moreover, the various States have been active on the regulatory front in terms of water sourcing and disposal for this very important energy sector. It was necessary to understand this dynamic nature of the shale gas market and the potential impact that has on the specifications and costs for our product water for frac re-use. The team reviewed information published in open literature and obtained feedback from frac operators. The team also visited frac flowback and underground injection disposal sites to get a better understanding of the operation logistics and specifications for water re-use.

Consequently, it became necessary to update the product water scope from the one product with 20,000 ppm TDS initially proposed to potentially four alternative products with varying levels of purification:

- Product-1: Clarified only (removal of suspended matter, free oil & grease, Fe, and microbiological contaminants)
- Product-2: Softened and Clarified (removal of hardness ions, namely Ba, Sr, Ca, Mg besides the purity specs for Product-1)
- Product-3: Partially desalinated to < 20,000 ppm TDS (besides the purity specs for Product-2)
- Product-4: Substantially desalinated to < 500ppm TDS (besides the purity specs for Product-2).

Product-3 above now represents the initial product target.

For this project, the verification of success criteria for critical go/no-go decisions were determined to be:

- Product quality specifications for the Products 1-4 to their respective target applications. Water recovery >95% for Product-1 and >90% for Product-2. For flowback water with <40,000 ppm TDS, water recovery > 50% for Product-3 and > 40% for Product-4.
- Cost of the overall Flowback Water Recovery Process (FWRP) < Cost of Conventional Saline Water Disposal. The FWRP includes Treatment Costs (mobile rig related process equipment, transportation & setup, chemicals and waste disposal, power) and Concentrate Disposal Costs. For the shale plays under consideration, this translates to target Treatment Cost < \$2/bbl flowback water.

- Separation process operable in a 50-gpm mobile rig configuration

Information on frac flowback attributes (flow rate vs. time and corresponding water analysis) is not readily available, as frac operators tend to keep their data proprietary and confidential. Nevertheless, relevant information on the flowback and produced waters in the Marcellus, Haynesville, Barnett, Fayetteville, and Woodford shales was acquired, albeit under non-disclosure agreements.

Flowback water is not a uniform “raw material” from a process development perspective. The physical and chemical properties of flowback water vary considerably depending on the geographic location of the shale play, the geological formation, and the chemicals introduced during the drilling and fracturing operations. Moreover, flowback volume and water properties vary throughout the lifetime of the well. The components in the flowback water of interest in this project are particulates (>5 µm), suspended solids (<5µm, colloids), free oil, dissolved organics, volatile organics, hardness ions (Ca, Mg, Ba, Sr, sulfates, carbonates), Fe, silica, and bacteria that may affect the product quality and/or the desalination membrane performance.

The flowback rate is highest initially and then decreases. Although there could be wide variation across geographical locations and due to operator bias, general flow profiles are shown below:

Time	Flowback rate	Flowback recovery, % frac fluid
1-5 days:	100-150 bbl/hr	10~ 25%
5-15 days:	20 – 60 bbl/hr	8 ~ 12%
15-30 days	5-10 bbl/hr	1~5%
30 - 90 days:	10 bbl/day	1~2%

The overall flowback after 90 days is in the range of 15~40%, but could be higher in certain wells.

Based on surveys of the TDS content of the flowback waters from the different shales, the team’s present view on the extent of applicability of our low-TDS (< 40,000 ppm) recovery approach is as follows: In Fayetteville and Woodford, almost 90-100%, since the flowback has generally < 40,000 ppm TDS. In Barnett, by selectively directing the flowback from the first 5 days, ~30-40% of the flowback may qualify as low-TDS, but recovery may not be considered at all since disposal via underground injection is readily and cheaply available. In Marcellus, overall only a small fraction (<10%) of the flowback may be amenable to low-TDS recovery. However, 10–20% of the flowback may be amenable at certain locations with appropriate water management to isolate the first 3~5 days of flowback water. In the Haynesville shale, due to the high TDS salinity and the availability of saline water disposal sites in East Texas, there is limited scope for membrane-based frac flowback recovery.

Frac flowback samples were obtained from wells in the Woodford shale in Oklahoma. These are daily samples from Day-1 through Day-14, along with two 55-gal drums of water samples from Day-1 and a composite of several daily samples. Another 55-gal drum sample was obtained from the Day-26 flowback from another nearby well. These water samples were used in experiments for assessing pre-treatment and membrane options.

Bench-scale experiments have been successful in identifying process technologies and associated operating conditions for the removal of key contaminants pursuant to the product quality specifications for the alternative Products-1, -2, -3 and -4. However, removal of organic contaminants proved to be a greater challenge for frac flowback waters than anticipated. This was solved with use of a novel ultrafiltration membrane. A novel analysis technique developed by Hans Grade at GE Global Research that uses a 2-column gas chromatography (GC) method for separation of the components

based on polarity and boiling point, followed by analysis with a Time of Flight Mass Spectrometer, was applied to understand the nature of organics in frac flowback water samples. This technique was found useful in providing a qualitative understanding of the effect of pretreatment methods on the presence and disappearance of organic compounds in the treated frac flowback waters.

For Products-3 and -4 that require RO membrane desalination, key membrane foulants, namely inorganic compounds that could physically precipitate inside the membrane module and inorganic and organic contaminants that could foul the membrane surface, were shown to be successfully removed in these bench-scale experiments. For demonstration, RO membrane fouling experiments were conducted using commercially available 2" diameter spiral wound RO modules with 10 liters of pre-treated Woodford Site-2 Day-26 35K ppm TDS flowback sample over 24 hours at 800 psig & 25C. The water-flux and salt-rejection vs. time profiles for this run were identical to those for a similar run with a "control" solution of 35K ppm TDS NaCl in deionized water. This indicated the effectiveness of the down-selected pretreated conditions in removal of potential membrane foulants.

For Product-3 and Product-4, various membrane system configurations were evaluated and optimized via performance modeling with GE Winflows software to increase water product recovery. For a feed solution composition similar to that obtained after pretreating (lime softened and filtered) Site-2 Day-26 sample, the identified configurations increased the recovery from 49% for a standard seawater-desalination design to as high as 61.5%. The maximum retentate concentration correspondingly increased from 68K ppm to 90K ppm TDS for these conditions. The increase in capital costs due to additional pumps, membrane modules, interconnected piping and controls for the new configuration were more than offset by the increased water recovery when the overall Flowback Water Recovery Process (FWRP) was considered.

Using the information from the bench-scale experiments for the various pretreatment steps, detailed conceptual flowsheets for the treatment processes were constructed for each of the Products 1-4 under consideration. These were evaluated for technical performance, costs and mobility for a 50-gpm feed (frac flowback) mobile rig system. Technical performance evaluation included mass and energy balances, including waste generation and handling. Costs included capital expenses for equipment and assembly and operating expenses for amortization of capital equipment, rig transportation and labor for rig-setup, chemicals, membranes, power, and waste removal. The cost estimations were based on reliable values obtained either from vendors or internal cost information for the desired equipment. Mobility included the preliminary assessment of the rig configurations and footprint suitable to treat 50 gpm of the frac flowback water.

The Treatment Cost target of <\$2/bbl was satisfied for all product options, in line with preliminary feedback on customer expectations. For the 50-gpm mobile rig configuration, the "fixed" expenses (capital-related costs, rig transportation & setup, maintenance) dominated the Treatment Costs at ~75% followed by chemicals & solids waste disposal at 18%, while the costs of replacement membranes and electrical power were only 2% and 5%, respectively

A value-assessment cost model was developed for the overall FWRP for the Products -3 &-4 that use RO membrane desalination to compare with the conventional disposal method. The conventional disposal cost included transportation of all flowback water and injection in Class II SWD wells while the FWRP cost included treatment costs, product delivery and remaining concentrate disposal (transport + SWD injection) costs. The sensitivities of the FWRP cost to prevailing concentrate disposal conditions were expressed as plots of  $C_{FWRP}/C_{Conventional}$  vs.  $C_{Disposal}$  at different feed TDS concentrations. The eco-

nomical “cut-off” TDS is defined as that feed TDS concentration when  $C_{FWRP}/C_{Conventional}=1$ . For Product-4 (500 ppm TDS), this “cut-off” TDS is in the range of 20,000 ppm to 65,000 ppm depending on the local saline water disposal costs. These sensitivity charts thus provide a means of comparing the relative value of FWRP for a well flowback treatment opportunity based on prevailing disposal costs and anticipated flowback TDS levels. Note that the other drivers, such as penalty avoidance or cost incentives due to frac flowback re-use due to local regulations have not been considered. In some cases, these non-technical issues may be the economic driver for FWRP.

To increase the overall system water recovery, a Hybrid membrane + thermal system was also considered. In this approach, the retentate (90,000 ppm TDS) from the membrane system is further concentrated by distillation in a mobile evaporator (such as that introduced by GE Water recently<sup>22</sup>) to yield a distillate with <500 ppm TDS but more importantly, a concentrate with 280,000 ppm TDS. The Hybrid system yields higher recovery; for example, 85% for a feed with  $y_F = 35,000$  ppm TDS vs. 61% for the membrane rig alone. However, the Hybrid process costs more than individual process options alone due to the high fixed costs for such small throughput (50 gpm) systems. The sensitivity plots of  $C_{FWRP}/C_{Conventional}$  vs.  $C_{Disposal}$  at different feed TDS concentrations show the dramatic decrease in  $C_{FWRP}$  for the Hybrid due to increased water recovery. The Membrane alone case is more economical for the lower  $C_{Disposal}$  cases mainly due to the lower overall capital costs. However, the Hybrid case becomes more economically attractive for the high  $C_{Disposal}$  (>\$5/bbl) shale plays where local SWD sites are unavailable, thus leading to higher flowback water transportation costs for the conventional disposal method.

It is concluded that membrane systems in combination with appropriate pretreatment technologies can provide cost-effective recovery of low-TDS frac flowback water for either beneficial reuse in hydrofracturing or safe surface discharge.

# 1 Project Narrative

## 1.1 Project Objectives and Approach

Two significant barriers to the development of many shale gas plays are water availability for drilling and hydrofracturing and disposal options for the water coproduced with gas ("frac flowback water"). In this project, GE Global Research (GEGR) evaluated technology that reduces the cost of treating flowback water for re-use in the hydrofracturing process.

The principal goal of this project was to define a mobile, cost-effective membrane-based process to treat low-TDS frac flowback water for re-use as hydrofracturing fluid. The TDS cutoff for consideration in this project is < 35,000 ~ 45,000 ppm, which is the typical limit for economic water recovery employing reverse osmosis (RO) type membrane desalination processes.

The conventional frac flowback water handling process, although quite complex in terms of the safety and operational logistics, is shown simplified for our purposes in Figure 1. The flowback water is directed to a separator to separate the water from the gas and the solid proppants. The flowback water is stored in interim storage tanks and then trucked to water disposal sites, typically Class II deep saline water disposal sites (SWD). At initial flowback rates, typically 100~150 bbl/hr, this translates to roughly one truck/hour for the first 5-10 days of flowback. This has implications for traffic, road infrastructure and noise pollution, as well as the loss of water from useful surface applications.

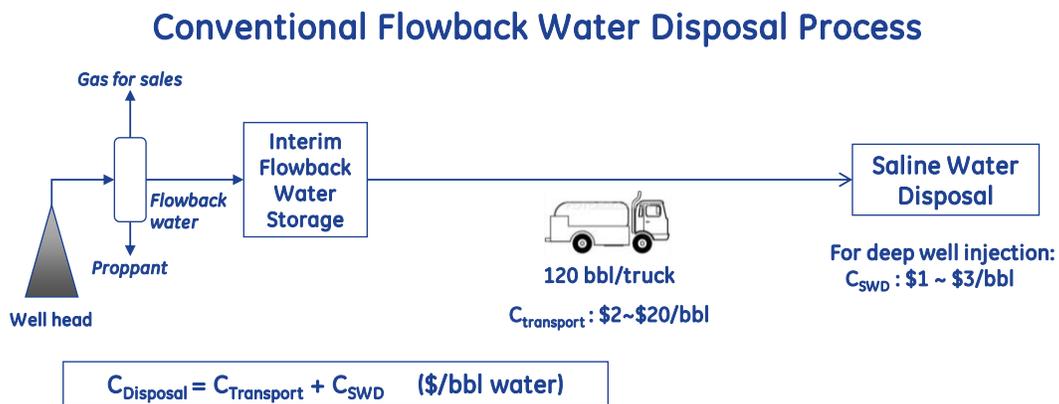


Figure 1 Simplified frac flowback water handling and disposal operation at a shale gas well site.

A conceptual process considered in this project for recovering all or part of the flowback water for re-use in hydrofracturing operations is shown in Figure 2. The flowback water recovery process (FWRP) is desired to be located physically close to the well operations to minimize water hauling costs. It includes a mobile unit equipped with the necessary treatment operations to provide "product" water that meets specifications for re-use in hydrofracturing. Only

a portion of the flowback water may be recovered as product, while the rest may have to be disposed of either in conventional saline water disposal Class II wells or via further recovery by methods suitable for desalination of high-TDS waters (> 80,000ppm), such as thermal processes.

## Flowback Water Recovery Process for Frac Re-use

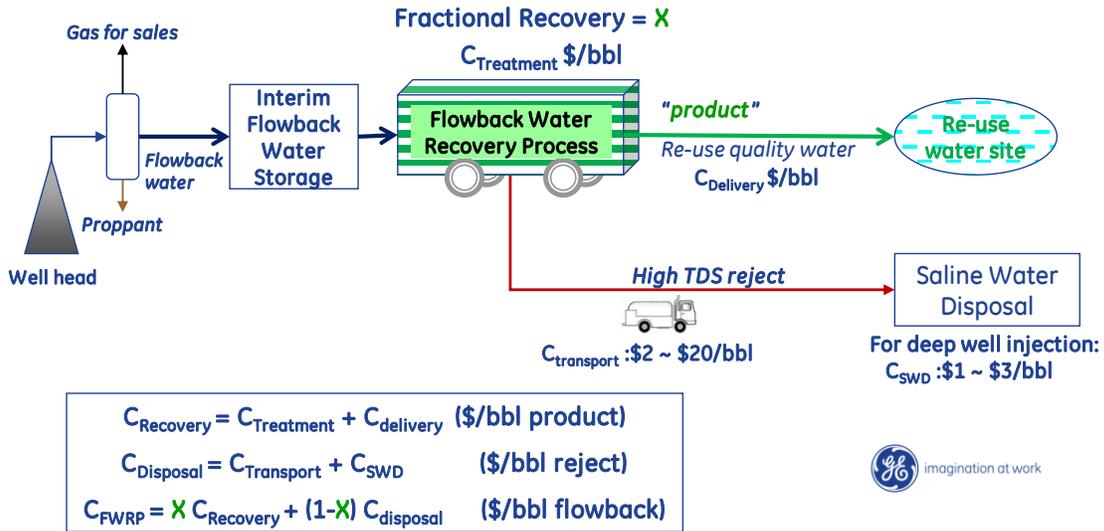


Figure 2. Conceptual Flowback Water Recovery Process (FWRP) for re-use in hydrofracturing. The overall cost will depend on the extent of water recovery, x, in the FWRP.

The chief benefits are greatly reduced fresh water consumption, up to 50% less water-transportation related traffic on roads, reduced water disposal costs, and a greatly reduced impact on the environment.

## 2 Budget

Budget Periods	Government Funding	GE GRC costshare amount	Total costs
10/1/2009 - 9-30-2010	\$ 628,075	\$ 157,019	\$ 785,094
10/1/2010 - 3/31/2011	\$ 152,769	\$ 38,192	\$ 190,961
TOTALS	\$ 780,844	\$ 195,211	\$ 976,055

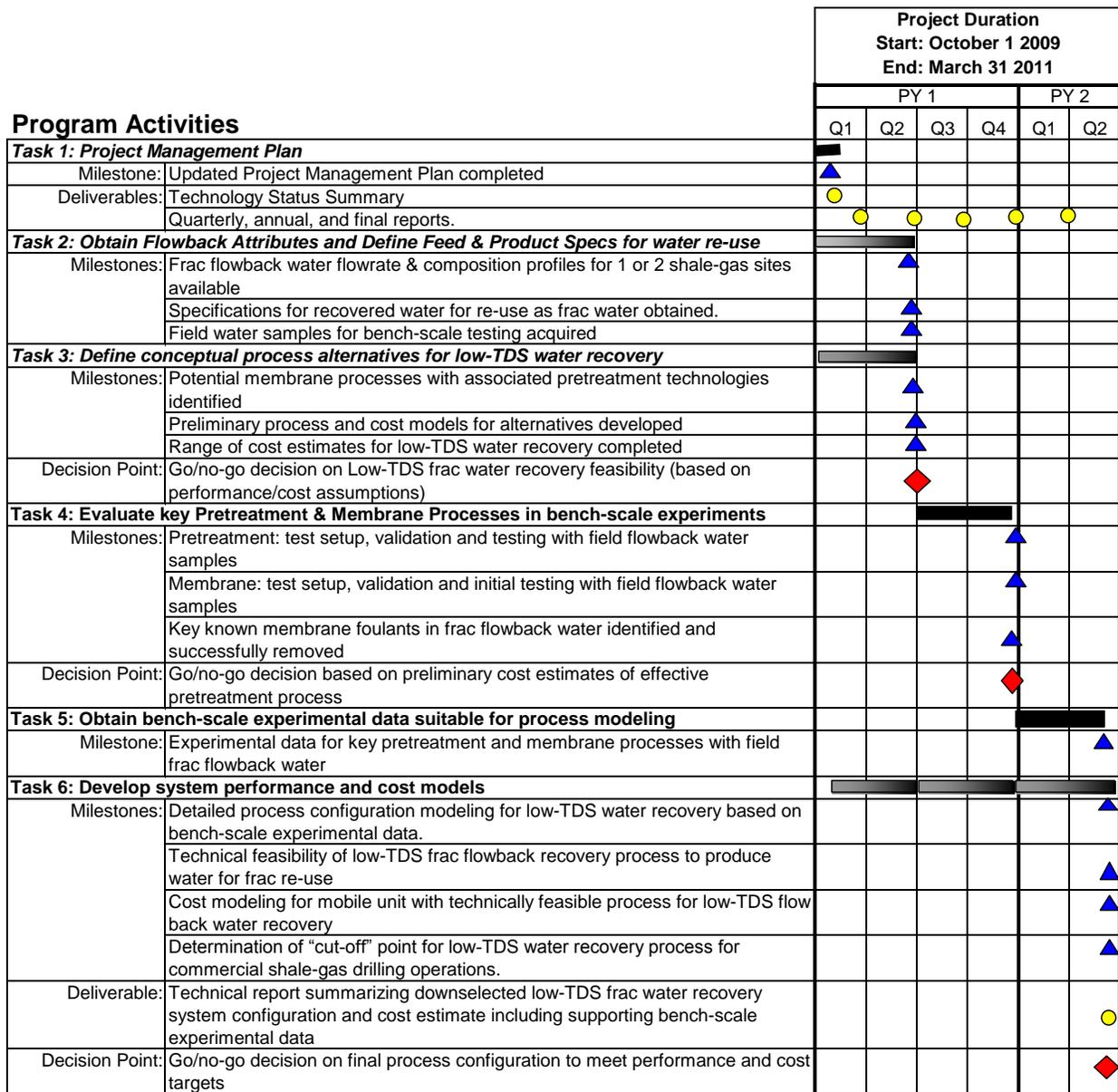
COST PLAN/STATUS												
Baseline Reporting Quarter	Year 1								Year 2			
	Q1		Q2		Q3		Q4		Q1		Q2	
	10/1/09 - 12/31/09		1/1/10 - 3/31/10		4/1/10 - 6/30/10		7/1/10 - 9/30/10		10/1/10 - 12/31/10		1/1/11 - 3/31/11	
	Q1	Total	Q2	Total	Q3	Total	Q4	Total	Q1	Total	Q2	Total
<b>Baseline Cost Plan</b>												
Federal Share	131,587	131,587	132,825	264,412	179,065	443,477	184,598	628,075	76,560	704,635	76,209	780,844
Non-Federal Share	32,897	32,897	33,206	66,103	44,766	110,869	46,150	157,019	19,140	176,159	19,052	195,211
Total Planned	164,484	164,484	166,031	330,515	223,831	554,346	230,748	785,094	95,700	880,794	95,261	976,055
<b>Actual Incurred Costs</b>												
Federal Share	68,328	68,328	163,173	231,500	149,290	380,791	97,508	478,299	104,443	582,742	145,448	728,190
Non-Federal Share	17,082	17,082	40,793	57,875	37,323	95,198	24,377	119,575	26,111	145,685	36,362	182,047
Total Incurred Costs	85,410	85,410	203,966	289,375	186,613	475,988	121,885	597,873	130,554	728,427	181,810	910,237
<b>Variance</b>												
Federal Share	(63,260)	(63,260)	30,348	(32,912)	(29,775)	(62,686)	(87,090)	(149,777)	27,883	(121,894)	69,239	(52,654)
Non-Federal Share	(15,815)	(15,815)	7,587	(8,228)	(7,444)	(15,672)	(21,773)	(37,444)	6,971	(30,473)	17,310	(13,164)
Total Variance	(79,074)	(79,074)	37,935	(41,140)	(37,218)	(78,358)	(108,863)	(187,221)	34,854	(152,367)	86,549	(65,818)

Total funding for this program was approximately \$1 MM including a 20% cost share contributed by GE Global Research, as seen in Table 1. Quarterly variances in spending were due to initial non-availability of frac flowback water samples. However, these mismatches were fully accounted for by the end of the program. Table 1 indicates that the program was under-spent by \$65K at the end of March 2011. However, final report and report-out is anticipated to bring this number to about \$20K which is within 2% of the original budget amount.

This project was organized into six interrelated tasks including:

- Project Management Plan
- Obtain flowback attributes (flow rate and composition profiles vs. time) and define specifications for water re-use
- Define conceptual process alternatives for low-TDS water recovery for re-use
- Evaluate key pretreatment and membrane processes in bench-scale experiments
- Obtain bench-scale experimental data suitable for process modeling
- Develop system performance and cost models for a mobile rig configuration of the downselected process to determine the commercial feasibility of the overall process for low-TDS flowback water recovery for reuse.

The project timeline and a task interrelationship chart summarizing the logic that connects the various tasks are shown in Figure 3 and Figure 4.



Legend: ● Deliverable    ▲ Milestone    ◆ Critical Path Milestone

Figure 3. Schedule and milestones for the program.

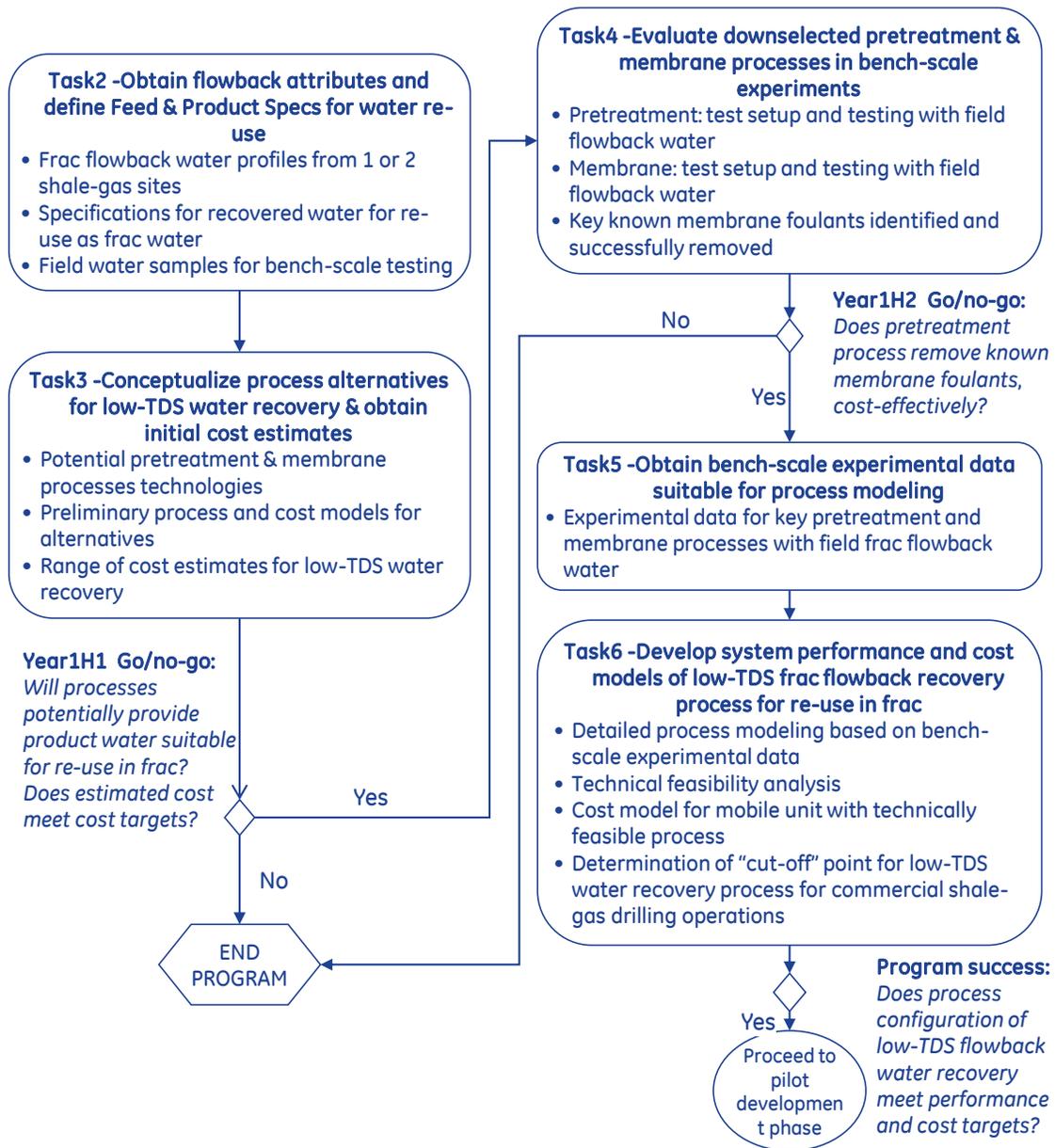


Figure 4. Task interrelationships and Go/No-go decisions.

## 3 Results and Discussions

### 3.1 Task 1: Project management

This program delivered 5 technical progress reports, one at the end of each quarter of this project. A Technology Status Assessment analyzing the most advanced examples of the proposed technology was completed and a report was issued. In addition, at the end of budget period (BP) 1 an annual report on project accomplishments for continuation of funding was submitted. The team presented work done for the project at the 2010 Ground Water Protection Council Annual Meeting, Pittsburgh, PA, Sep 26-28<sup>1</sup> and the Canadian Society of Unconventional Gas Water Workshop, April 20, 2011<sup>2</sup>. Additionally, presentations were made to potential customers to educate and highlight potential solutions to frac flowback and produced water recovery.

### 3.2 Task 2: Obtain Flowback Attributes and Define Specifications for Water Re-use

#### 3.2.1 Objectives and Approach

The specific objectives of this task were to:

- Understand frac flowback operations and estimate the amount of flowback that qualifies as “low-TDS” water suitable for recovery via membrane processes
- Define performance and cost specifications, and develop the verification of success criteria for assessing the water recovery processes considered in this project.

The key activities were to:

- Obtain frac flowback water attributes (composition and flow rate profiles over time)
- Obtain specifications for “product” water that would be re-used for hydrofracturing.

We reviewed information published in open literature, discussed with frac operators, and visited a frac flowback site to get a better understanding of the actual operation logistics.

There have been several barriers to obtaining reliable information on the water chemistry used for hydrofracturing, flowback attributes, and specifications for the re-use water, including:

- The water chemistry used for hydrofracturing depends on the geology of the shale formation and the technology bias/experience of the operator. Thus, there could be variation in the water chemistry between different shales, within different sites within the same shale and between different services companies operating in the same shale. Moreover, the methods used for hydrofracturing are being continuously updated as the industry tries to optimize operations to maximize gas recovery while minimizing energy and especially, fresh water usage<sup>3</sup>. For example, current research

on new slicking agents (friction reducers) may allow the use of higher salinity in the feed water compared to present operations.

- Information on frac flowback attributes (flow rate vs. time and corresponding water analysis) is not readily available, as frac operators tend to keep their data proprietary and confidential. There is very limited published data on the flowback attributes for the various shales.
- Opinions vary widely on the water quality that may be used for hydro-fracturing. For instance, some of the operators insist on using very low-TDS source water to avoid scaling issues in the downhole piping, while others, such as Range Resources, have reported some success in using a 26,000 ppm Chlorides water feed in the Marcellus shale<sup>4</sup>. Some experts feel that water salinity equivalent to seawater, namely ~ 35,000 ppm TDS may be usable for hydrofracturing<sup>5</sup>. Some operators are considering the use of even salinity as high as 120,000 ppm TDS with low hardness and scale-causing contaminants<sup>6</sup>. As a practical matter, the relative costs for drilling and hydrofracturing a well are in the neighborhood of \$1million each, while water costs for 100,000 bbls, when available, are in the neighborhood of \$25,000. The risks associated with scaling and well-plugging due to “unclean” water used for hydrofracturing may not be tolerable to many operators. Hence, it appears that the move towards higher TDS water used to stimulate gas wells is being driven by state and regional water availability, the logistics of flowback water transportation and disposal costs, and also the desire to mitigate negative public perception about water use for hydrofracturing and groundwater pollution.
- Regulations are being considered by various federal and state agencies on the disclosure of chemistry used for the hydrofracturing process, discharge of flowback water, and the re-use of flowback water for hydrofracturing. Until the regulations are finalized, there will be uncertainty on the specifications for the treated water and discharge water. This affects the determination of how much of the flowback water would qualify as “low-TDS” suitable for membrane treatment, the choices of technology options useful to treat the frac flowback water to meet the technical specifications, and the overall system cost.

The conclusion from our survey was that the specification for acceptable re-use is **subject to change in the short-term** depending on technology advances that are continuously occurring, operator experience and confidence, and upcoming regulations regarding discharge and re-use.

Nevertheless, we were able to find relevant information on the flowback and produced waters in the Marcellus, Haynesville, Barnett, Fayetteville and Woodford shales. Some of this data was acquired under non-disclosure agreements and will only be summarized as appropriate in the following sections.

### 3.2.2 Water usage in shale gas exploration

The main uses for water in deep shale exploration are:

- Drilling, where a mixture of clay and water is used to carry rock cuttings to the surface, as well as to cool and lubricate the drill bit.
- Hydrofracturing (or “frac”), where a mixture of water and sand is injected into the deep shale at a high pressure to create small cracks in the rock and allow gas to freely flow to the surface.

Typical average usage of water for drilling and frac operations for the Barnett, Fayetteville, Haynesville and Marcellus shales, as estimated by Chesapeake Energy Company<sup>7</sup> are shown in Table 1.

**Table 1. Water usage (average) per well and water requirements for the various shale plays (as estimated by Chesapeake Energy<sup>7</sup>)**

	Water used (average), bbls/well			Wells/year	Water MM bbls/year
	Drilling	Fracturing	Total		
<b>Barnett</b>	10,000	70,000	80,000	600	48
<b>Fayetteville</b>	1,500	70,000	71,500	250	18
<b>Haynesville</b>	25,000	65,000	90,000	200	18
<b>Marcellus</b>	2,000	90,000	92,000	600	55

According to Chesapeake Energy, a deep shale gas well will produce between 2 and 6.5 Bcf (billion cubic feet) over its lifetime. Thus, the amount of water used to produce the gas equates to about 0.8 to 1.7 gallons/MMBTU or 19 to 40 bbls water/MMcf of gas (assuming 1,000 scf of gas is equivalent to 1 MMBTU of energy)<sup>8</sup>.

### 3.2.3 Definitions of various fluids used in shale gas exploration – Fracturing, Flowback/Produced waters

The fluid that is used to stimulate the shale gas formation during hydrofracturing is generally referred to as “Fracturing Fluid” or “Completion Fluid”. The fluid that flows back after a hydrofracturing operation is referred to either as “flowback” water or “produced” water. There is some confusion on the strict definitions and differences between the two terms. In conventional oil & natural gas fields and in coal bed methane reservoirs, there is an excess of water in the formation that comes up to the surface during oil and gas production. This water has traditionally been referred to as “produced water”. In fact, during oil production, it is estimated that approximately 7 bbls of water are produced for every bbl of oil<sup>9</sup>. However, in shale gas exploration, typically, most of the water that flows back is the water that was fed during the hydrofracturing operation.

According to Horn<sup>10</sup>, when the flowback volume reaches 100% of the fracturing fluid volume, it is then subsequently referred to as “produced water”. However, our survey<sup>11</sup> of gas pro-

ducers appears to indicate that the rationale for referring to the water as “flowback” or “produced” could be any of the following:

1. Financial: Water produced during the well completion stage is defined as flowback and the associated costs are part of the well completion budget. When the well is considered to be under “gas production” the water is called “produced”, and the associated costs are part of the “operating” budget.
2. Time: Some companies use a time factor, for example 30 days as the demarcation between “flowback” and “produced”. Typically, the flow rate has dropped off significantly during this period.
3. Volume: Some producers differentiate based on how much they get back as a percent of fracturing fluid put down into the well. It may be 100% as per the definition provided by Horn<sup>10</sup> or less, as per the operator’s choice. However, in shale gas wells, the overall water flowback could be < 50% of the fracturing fluid used, typically only 25-35% in the first 30 days.

It appears that the financial reason appears to be the most commonly used definition to differentiate between “flowback” and “produced” waters.

In any case, for shale gas wells, from a flow rate perspective, the flow rates during the “flowback” phase are significantly larger (by 10-100x) than in the “produced” phase. From a chemical perspective, the produced water has higher concentrations of the various minerals because of the greater residence downhole, whereas the flowback water may contain higher amounts of suspended solids, oils, fuels and chemicals associated with the drilling and hydrofracturing operations. However, for some shales, the chemical characteristics during the flowback phase may have already approached those at the produced phase of the operation (depending on the definition chosen by the operator).

In this report we do not differentiate between the two definitions and refer to all returning water after a hydrofracturing event as “flowback” for evaluation of our recovery process options.

### **3.2.4 Water Chemistry of the fracturing fluids used for shale gas exploration**

It is important to know the composition of the fluid used for drilling and hydrofracturing since the flowback water may contain some or all of these chemicals besides the contaminants from the soil and shale layers.

#### Drilling fluids:

The composition of the drilling fluids used depends on the geology of the shale formation and the technology bias/experience of the operator. Most of the information is held proprietary and confidential. However, a good summary of the various components is provided at the

DOE NETL website<sup>12</sup>. Relevant information for this project is summarized in Appendix A. From the flowback water treatment perspective, the key components that could be considered as contaminants during recovery are:

- “oil” in the oil-based muds. These are most likely diesel. In fact, the Day-1 sample of flowback water obtained by the team has a diesel-like odor. Apparently, at some locations, after drilling, the equipment are cleaned with diesel, although this practice may be discontinued in the future<sup>13</sup>.
- olefins, esters, linear alpha-olefins, poly alpha-olefins, linear paraffins, etc. in the synthetic-based muds, if used.

#### Frac fluids:

Fracturing fluids used for fracturing gas shales include a variety of additive components, each with an engineered purpose to facilitate fractures and the production of gas<sup>3</sup> (see Appendix for details). Currently, the trends in shale wells are to use water based or mixed slick-water-fracturing fluids. These are water-based fluids mixed with friction reducing additives<sup>14</sup>, which allows a fracturing fluid and proppant to be pumped to the target zone at a higher rate and reduced pressure than by using water alone. In addition, other additives including biocides are utilized to prevent micro-organism growth and to reduce bio-fouling of fractures. Of particular concern are the sulfate reducing bacteria (SRB) as they reduce sulfate ions to hydrogen sulfide; H<sub>2</sub>S causes corrosion in the downhole pipeline and at higher concentrations (> 4 ppmv) may cause sourness issues with the sales gas. Oxygen scavengers and other stabilizers which prevent corrosion of metal pipes and acids which are used to remove drilling mud damage near the wellbore area are also common either in fracturing fluids or as part of fracture treatments.

Details of the various components in the hydrofracturing fluid are provided in Appendix. From the flowback water treatment perspective, although it is expected that some or all of these additives may be expected in the flowback, no literature reports confirming the presence and concentrations of these additives could be found. It is likely that these compounds may get chemically, physically or microbiologically altered or destroyed during the hydrofracturing process or become lost in the shale formation. Although some of these additives, such as guar gel, polyacrylamides, and petroleum distillates, may affect membrane performance, the actual impact would have to be experimentally determined with flowback water samples.

#### **3.2.5 Flowback Attributes**

Information on frac flowback attributes (flow rate vs. time and corresponding water analysis) is not readily available, as frac operators tend to keep their data proprietary and confidential. There is very limited published data on the flowback attributes for the various shales. Nevertheless, we were able to find relevant information on the flowback & produced water attributes for the Marcellus, Haynesville, Barnett, Fayetteville and Woodford shales. Most of this

data was acquired under non-disclosure agreements and will only be summarized, as appropriate in the following sections.

### Flowback Flow rates

For the Marcellus shale, Gaudlip<sup>4</sup> has reported flowback volumes over a period of 14 days for a few wells, as reproduced in Figure 5.

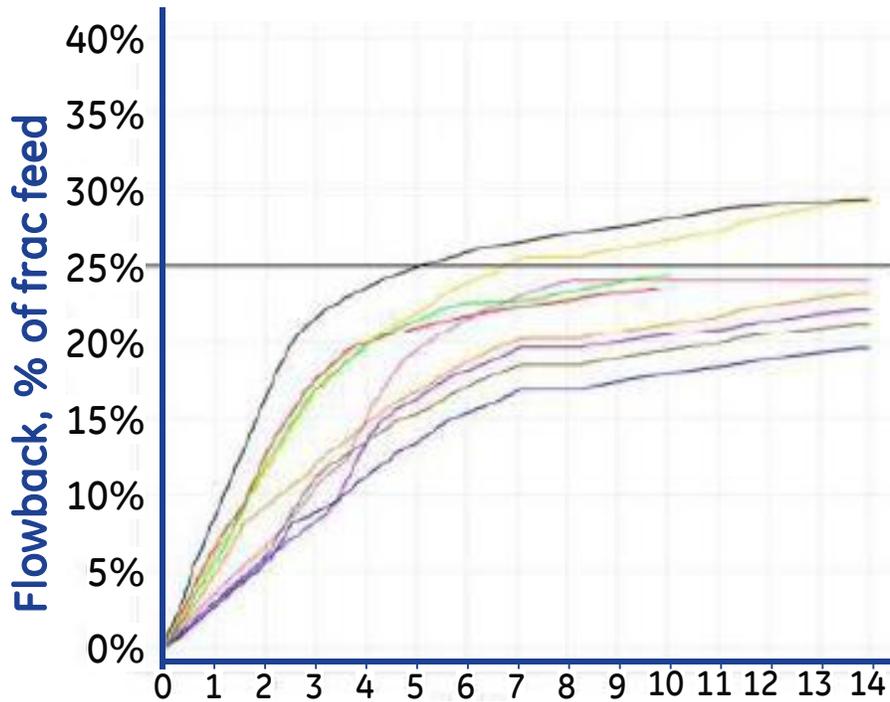


Figure 5. Flowback from a few wells in the Marcellus shale (Gaudlip et al).

We make the following observations:

- The % recovery, i.e. the volume of water that flows back as a % of the fracturing fluid fed during the hydrofracturing process is between 19% to 29% at the 14-day mark. A general rule of thumb is that ~25% recovery is the expected norm in the Marcellus shale during the initial phase of the flowback, generally regarded as the first 30 days<sup>11</sup>.
- The flowback rate is highest initially and then decreases. This is illustrated in Figure 6. For the first few days, the flow rates could be in the high range of 2,500 to 6,000 bbls/day (or ~100 bbls/hr to 250 bbls/hr). There is a significant drop off in the flow rate at or near the 10 day mark to ~ 1000 bbl/day (or ~ 40 bbl/hr), and another significant drop at the 30 day mark to ~100-150 bbl/day (or 4 to 6 bbl/hr). Beyond the 50-day mark, the flow rates are between 5 to 100 bbl/day but mostly ~ 10 bbl/day (or 0.4 bbl/hr).

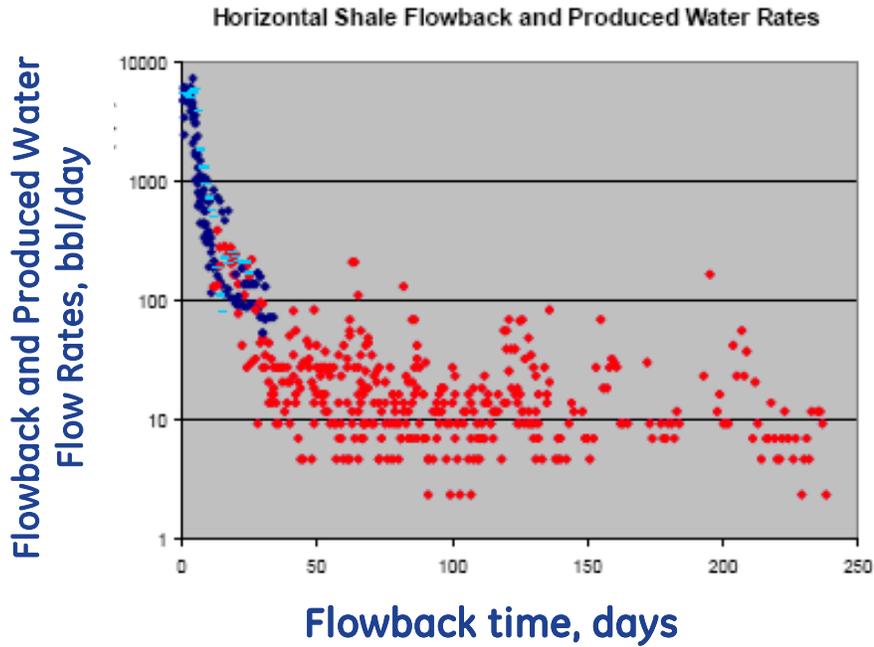


Figure 6 Flow rates vs. Flowback time for a few wells in the Marcellus shale (Gaudlip<sup>4</sup>). Blue points refer to "Flowback" and the red points refer to "Produced".

Horn<sup>10</sup> has reported flowback attributes for a Woodford shale site. Their flow rate data is re-plotted in Figure 7. We again observe that the flow rate was ~ 150 bbl/hr for the first 3 days and then decreased with time. At the 10-day mark, the flow rate was ~ 50 bbl/hr. In this case, at the 14-day mark, only ~34% of the ~95,000 barrels used for hydrofracturing had been recovered.

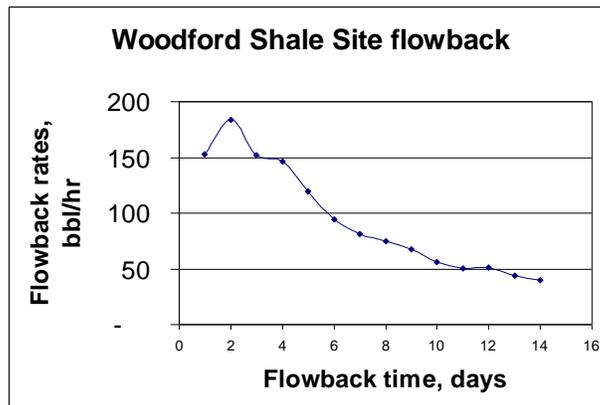


Figure 7. Flowback rate vs. time for a Woodford shale (re-plotted from the data shown in Horn<sup>10</sup>).

In Figure 8, typical flowrates for the Woodford that were shared by a customer are shown. We see that the flowrate profiles for two of the wells are similar as in Figure 7 while the flowrate decreases rapidly for one of the wells.

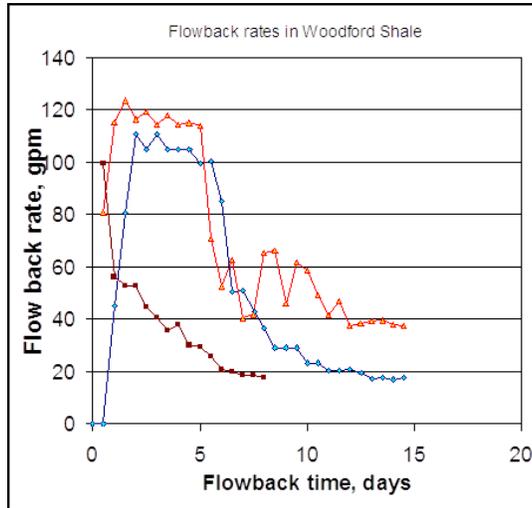


Figure 8. Flowrate profiles for frac flowback from three Woodford shales.

#### Flowback Composition

For the **Marcellus** shale, the flowback compositions for a few sites have been reported by Gaudlip<sup>4</sup>. The composition of a flowback sample from a Marcellus shale site is reproduced in Figure 9.

Cations		mg/L
Calcium (Ca <sup>2+</sup> )		20,463
Magnesium (Mg <sup>2+</sup> )		1,987
Sodium (Na <sup>+</sup> )		37,063
Iron (Fe <sup>2+</sup> )		143
Potassium (K <sup>+</sup> )		296
Barium (Ba <sup>2+</sup> )		203
Strontium (Sr <sup>2+</sup> )		2,243
Manganese (Mn <sup>2+</sup> )		43
Anions		mg/L
Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )		100
Sulfate (SO <sub>4</sub> <sup>-</sup> )		8
Chloride (Cl <sup>-</sup> )		97,084
		mg/L
TDS		159,541
Gases		mg/l
Carbon Dioxide (CO <sub>2</sub> )		481
Hydrogen Sulfide (H <sub>2</sub> S)		2

Figure 9. Composition of a flowback sample from a Marcellus shale site (reproduced from Gaudlip<sup>4</sup>).

Although the TDS of ~ 160K ppm of this particular sample is too high for any reverse-osmosis membrane based recovery processes, there are some interesting observations to be made, as described below.

- The chlorides concentration at ~97K ppm make up ~60.6wt% of the TDS. Interestingly, this value is remarkably close to the value of 60.8 wt% that we would obtain if we assume that the TDS were entirely due to NaCl (based on the ratio of molecular weights,  $M_{Cl}/M_{NaCl} = 35.5/58.5 = 0.608$ ). However, note that the Na content in Figure 4 corresponds to only 23.2wt% in the flowback sample vs. 39.2wt% in pure NaCl.
- The concentration of the “hardness” ions (divalents – Ca, Mg, Ba, Sr) correspond to ~56K ppm when reported on a CaCO<sub>3</sub> basis. The ratio of Hardness (CaCO<sub>3</sub> basis)/TDS = 56K/160K ~ 0.35. This value is in close agreement with several other data that we have examined for the Marcellus shale. This ratio varies amongst different shales with values ranging from 0.2 to 0.35 depending on downhole soil conditions and the composition of the water used for hydrofracturing.
- The source of potassium is perhaps from KCl added to the fracturing fluid during hydrofracturing. So, it may be desirable to retain it in the product water for frac re-use.
- The Sulfates concentration is low at ~ 8 ppm. This is not surprising since the Ba and Sr concentrations are so high at 203 and 2243 ppm, respectively. This also implies that most of the divalents and trivalent ions are present in the form of chlorides that have higher solubilities in water in relation to NaCl.
- The Fe content of 143 ppm may be too high for re-use, especially since it is in the Fe<sup>2+</sup> state, which may potentially get oxidized and form undesired precipitates that could cause scaling.

Gaudlip<sup>4</sup> has also reported on the variation of chloride concentration in the flowback as a function of flowback time, as reproduced in Figure 10. From our general observation noted earlier of the relationship between Cl and TDS in flowback waters, we may obtain a rough estimate of the TDS by dividing the Cl values by 0.61. From Figure 10, we note that in the Marcellus shale, the Cl values rise quickly, as follows:

	Cl, ppm	Estimated TDS, ppm
Day 5:	20K to 70K	33K to 115K
Day 10 :	40K to 90K	66K to 148K
Day 15:	55K to 110K	90K to 180K

From the above data, we observe that the “low-TDS” water recovery processes (<45,000 ppm TDS in flowback) may have limited applications in the Marcellus shale play. However, we observe from composition data obtained from elsewhere in the Marcellus shale play from con-

Confidential sources, that 10-20% of the flowback may be amenable at certain locations with appropriate water management to isolate the first < 3~5 days of flowback water.

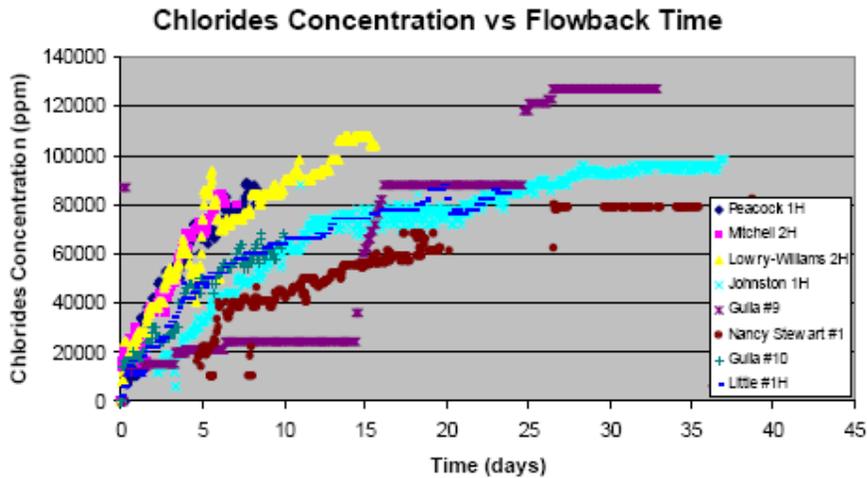


Figure 10. Variation of flowback composition with time for a Marcellus shale site (reproduced from Gaudlip)

For a **Haynesville** shale site, Kaufman et al<sup>15</sup> have described the flowback composition. The data for the sulfates and Ba/Sr compositions plotted as a function of the cumulative flowback volume are reproduced in Figure 11. We observe a sharp transition at ~ 11,000 bbls when the Ba/Sr concentrations increase to cause a precipitous drop in Sulfate concentrations.

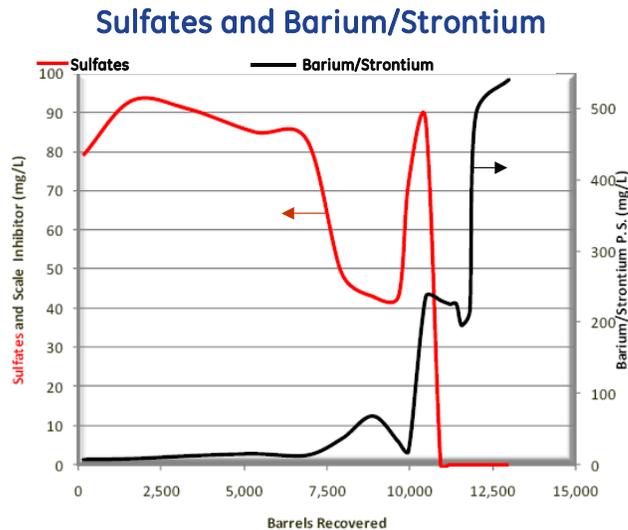
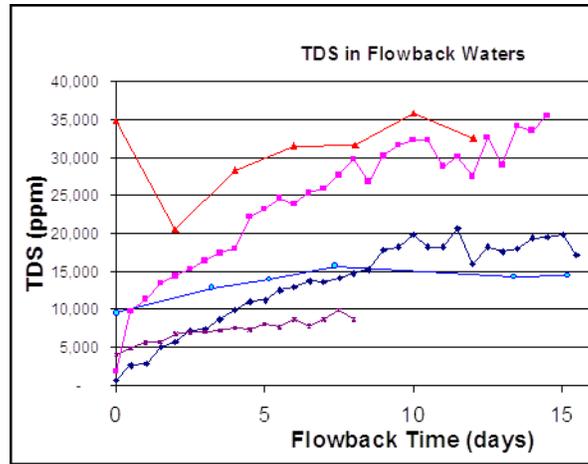


Figure 11. Variation of Sulfates and Ba/Sr concentrations as a function of flowback volume for a Haynesville shale

For the **Woodford** shale, Total Dissolved Solids (TDS) concentration profiles for a few wells are shown in Figure 12. We observe that the concentrations increase from nearly zero initially to between 15,000 ppm to 35,000 ppm over the next 15 days.



**Figure 12. Total Dissolved Solids (TDS) concentration profiles for flowback waters from a few Woodford shale wells**

### 3.2.6 Summary of the flowback attributes

Flowback water is not a uniform “raw material” from a process development perspective. The physical and chemical properties of flowback water vary considerably depending on the geographic location of the shale play, the geological formation, and the chemicals introduced during the drilling and fracturing operations. Flowback volume and water properties vary throughout the lifetime of the well.

### 3.2.7 Flowback volumes amenable to “Low-TDS” membrane-recovery

*Flowback waters with composition in the <45,000 ppm range are highly amenable for economic recovery using RO-based membrane recovery systems.*

The initial flowback typically has low enough salinity to qualify for recovery via the methods that were investigated in this project. However, as noted earlier, the TDS levels increase with flowback volume, and the rate of increase depends on the shale formation, the TDS of the water used for hydrofracturing, etc. Based on our survey of available literature information, the salinity ranges of the flowback waters from the various shales are shown in Table 2. The average values represent a combined mean for flowback from a well while the maximum could be an instantaneous value. Note that the actual values will vary widely from the numbers given here depending on the well location, chemistry, etc.

**Table 2. Salinity of the flowback waters from various shales expressed in terms of Total Dissolved Solids (TDS).**

<b>Shale</b>	<b>Average TDS, ppm</b>	<b>Maximum TDS, ppm</b>
Fayetteville	13K	20K
Woodford	30K	40K
Barnett	80K	>150K
Marcellus	120K	>280K
Haynesville	110K	>200K

The extent of applicability of our low-TDS recovery approach for the various shales would be ~100% of the flowback from the Fayetteville and Woodford shales. In the Barnett shale, by selectively directing the flowback from the first 5 days, ~30-40% of the flowback may be amenable to the Low-TDS recovery (note, however, that this recovery process may not be considered at all since deep well disposal is easily available and so cheap - unless water availability may be an issue due to drought conditions). In the Marcellus shale, overall, only a small fraction (<10%) of the flowback may be amenable to Low-TDS recovery; however, 10-20% of the flowback may be amenable at certain locations with appropriate water management to isolate the first 3~5 days of flowback water. In the Haynesville shale, due to the high TDS salinity and the availability of saline water disposal sites in East Texas, there is limited scope for membrane-based frac flowback recovery.

### **3.2.8 Flow volumes & flow rates**

The amount of frac fluid used depends on the type of well, the geographical location and operator bias/experience:

<u>Well type</u>	<u>Range</u>	<u>Mean</u>
Vertical	11,000 – 90,000 bbls	40,000 bbls
Horizontal	70,000 – 190,000 bbls	100,000 bbls

Flow rates during flowback typically show the following characteristics as a function of flowback time:

<u>Time</u>	<u>Flowback rate</u>	<u>Flowback recovery, % frac fluid</u>
1-5 days:	100-150 bbl/hr	10~ 25%
5-15 days:	20 – 60 bbl/hr	8 ~ 12%
15-30 days	5-10 bbl/hr	1~5%
30 - 90 days:	10 bbl/day	1~2%

%flowback after 90 days: 25~40%, but could be higher in certain wells.

However, it is important to note that there is considerable variation in the flow rate profiles during flowback, and the water recovery cleanup system needs to be robust to these flow fluctuations.

### 3.2.9 Frac site visit

We visited a frac site in the Barnett shale in Fort Worth, TX area to get a first-hand understanding of the flowback operations and the water-handling logistics. Due to safety concerns, we could not visit this site during the hydrofracturing process but our visit happened immediately after the “frac-job” and while the well services crew was managing the flowback. We also visited a saline water deep well injection site in the Cleburn, TX area. In Figure 13, the photograph shows a saline water disposal (SWD) well co-located with three hydrofractured wells producing gas. At this site, the saline water was being disposed into the Ellenburger formation that was below the shale-gas formation layer. One of the remarkable impressions of these site visits was the general cleanliness of the operational sites once the flows were established.



**Figure 13. Photograph shows a saline water disposal (SWD) well co-located with three hydrofractured wells. At this site, the saline water was being injected into the Ellenburger formation that is below the shale-gas formation layer.**

### 3.2.10 Flowback samples

It had been challenging to obtain water samples from frac flowback, as frac operators prefer to keep the information proprietary and confidential. After several months of trying, we were fortunate to obtain flowback samples from two wells in the Woodford shale in Oklahoma. The well was hydrofractured in mid-March, 2010. For client confidentiality reasons, the customer and sites will not be identified in this report. The sample collections from the sites were as follows:

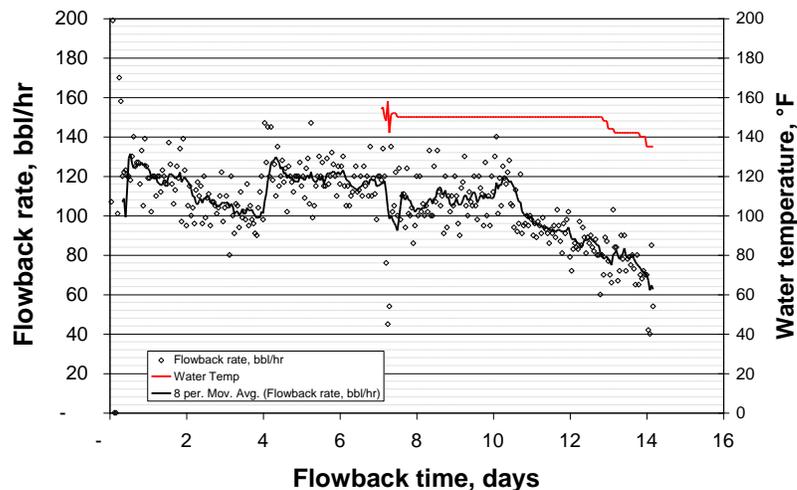
- Site-1: We coordinated with the customer to collect water samples during the initial flowback.
  - Daily 1-liter samples were collected from Day-1 through Day-14
  - One 55-gal drum from Day-1. This is referred to as “Site-1 Day-1” sample.
  - One 55-gal drum containing a composite of several daily samples. This is referred to as “Site-1 Composite” sample.

- Site-2: One 55-gal drum of sample was collected on the Day-26 after flowback had started. This is referred to as “Site-2 Day-26” sample.

In the sections below, the variation of frac flowback flow rate and the concentrations of the various components/contaminations in the above mentioned flowback waters are discussed.

### 3.2.10.1 Flowback rate profile

The profile for the flowback rate for Days 1-14 at Site-1 is shown in Figure 14. We observe the highly varying nature of the flowrate profile on an hourly basis. Over the first 11 days, the flowrate is approximately constant at about 120 +/- 15 bbl/hr. Beyond Day-12, the flowrate appears to decrease with time. Interestingly, the flowrate profile at this Site-1 is different from the profiles shown in Figures 7 and 8, also for wells in the Woodford shale, wherein the flow rate drops steeply over the first 10 days of flowback from ~150 bbl/hr initially to ~ 50 bbl/hr. This illustrates one of the key issues with frac flowback water treatment, especially for



**Figure 14. Profiles of the flowback water rate and water temperature are plotted vs. flowback time for the Site-1 in Woodford shale.**

an on-site mobile rig that will have to be robust to such varying flow profiles not only at the same frac sites but also that anticipated across different frac sites, although in the same shale geology.

### 3.2.10.2 Flowback Temperature:

In Figure 14, the temperature profile for the flowback water from Site-1 is also plotted. We note that the temperature is about 150°F. The flowback water temperature varies across frac sites and with time. Water from deeper wells tends to have higher temperatures. Also, the temperature is higher initially when the flowback rates are highest and gradually decreases with time. This relationship is apparent in the flow rate and temperature profiles in Figure 14. This aspect of the flowback has implications on the choice of process technologies and design of on-site mobile rigs to make them robust to varying temperatures; alternatively,

we may need to install adequate heat exchange equipment if the chosen treatment processes have limited temperature operating ranges.

### 3.2.10.3 Flowback Water Composition

The water samples were analyzed at the GE Water Analysis Lab, Woodlands, TX, employing standard techniques used routinely for analysis of frac flowback and produced waters. The compositional data for the various components of interest are shown below in Figures 15-23.

#### Total Dissolved Solids (TDS)

The TDS values for Woodford Sites 1 and 2 are plotted in Figure 15. The TDS profile for Site-1 Days 1-14 was surprising. The Day-1 sample had ~ 38,000 ppm TDS and the value climbed up to ~ 85,000 ppm TDS on Day-14. This is in contrast to all the other data we had seen from customers in the Woodford shale, wherein the general trend showed that the TDS after Day-14 was between 10,000 and 38,000 ppm, as seen in Figure 12. Interestingly, the Day-26 sample from Site-2 had ~35,000 ppm TDS, which is in agreement with the general trend. Horn<sup>10</sup> has reported a value of ~13,800 ppm TDS for a Woodford shale site flowback water. It is not known why the Site-1 flowback shows such elevated levels of TDS.

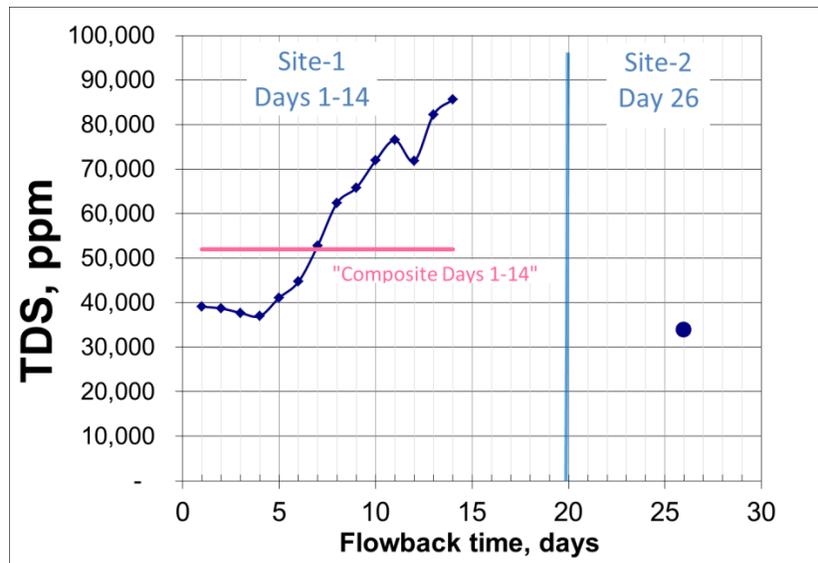


Figure 15. Concentration profiles for Total Dissolved Solids (TDS) for the two Woodford frac sites.

#### Total Suspended Solids (TSS)

These are fine particulates of inorganic, metallic or organic materials, typically < 5 µm in size. They can also be colloidal in nature. The TSS measurement is conducted by passing the water sample through a 1.0 micron filter and weighing the residue material after drying. Turbidity, measured and reported in NTU units, refers to the transmission (or lack of) of light

through a water samples. Turbidity may be influenced by the suspended solids and also color of the sample.

In Figure 16, the TSS and Turbidity profiles for the Woodford Sites 1 and 2 are plotted. We note that the TSS generally decreases as a function of flowback time for Site-1 flowback from as high as ~825 mg/l on Day-1 to below detection. Interestingly, the Site-2 Day-26 sample also had low TSS values. Many of the produced waters (late flowback) obtained from other shales also typically show very low TSS values.

The Turbidity values, however, show a changing profile as a function of flowback time for the Site-1 flowback. This observed change in Turbidity (NTU) measurements may be influenced by the sample color. The Day-26 sample from Site-2 shows a value of ~ 300 NTU, which is in the range of the values measured for the Site-1 Days 1-14 flowback.

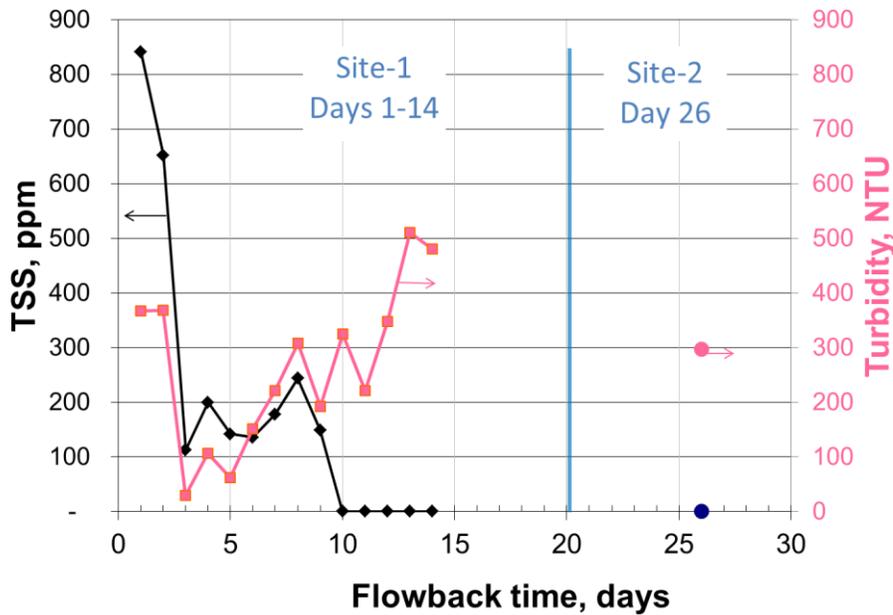


Figure 16. Concentration profiles for Total Suspended Solids (TSS) and Turbidity for the two Woodford frac sites.

Organics:

The organic content of the flowback waters was measured by two techniques, namely via “hexane extraction” and by Total Organic Carbon (TOC). The “Hexane Extractables” method gives a measure of the components that are hexane soluble and is a good indicator of the free Oil & Grease content of the frac flowback water. The TOC measures the amount of combustible organic carbon present in the frac flowback water and is an indicator of dissolved and undissolved organics, including non-volatile and volatile compounds. Chemical Oxygen Demand (COD) is typically also mentioned in such water analyses; however, the presence of high amounts of chlorides interferes with this test and gives inaccurate results, and hence is not reported here.

The profiles for the Hexane Extractables and TOC for the flowback waters for the Woodford Sites 1 & 2 are plotted in Figure 17. For the Site-1 flowback over Days 1-14, we observe high initial values for Hexane Extractables followed by a sharp decrease over the next few days. The values are below detection beyond Day-10 for Site-1 which also corresponds to negligible value for the Day-26 sample from Site-2. The TOC profile for the Site-1 Days 1-14 samples also shows a high initial value of ~ 180 mg/l for Days 1 & 2 followed by a sharp decrease over Days 3 & 4, but then increases to a value of ~ 30 mg/l over the next few days. The value for the Day-26 sample from Site-2 is ~ 18 mg/l. It is likely that the Site-2 flowback may have gone through a similarly varying profile before settling to a steady value.

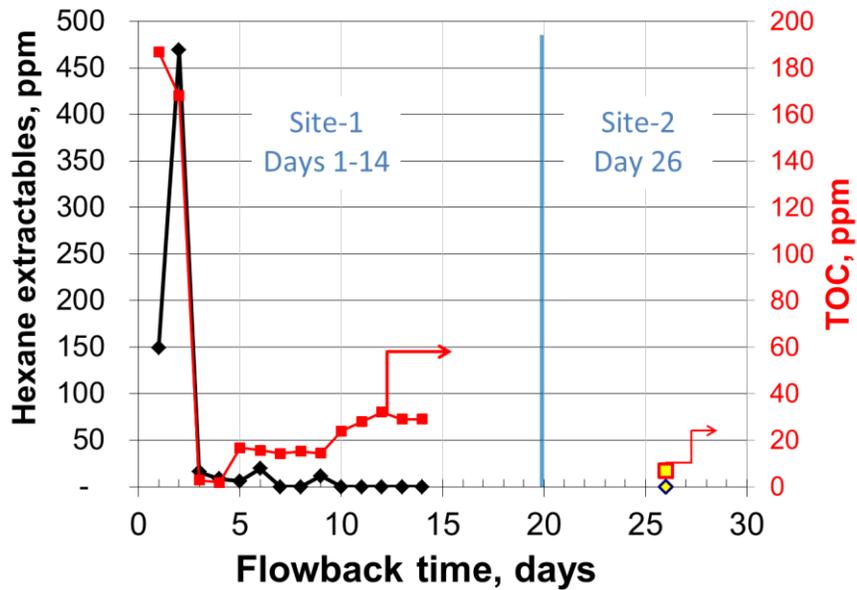


Figure 17. Concentration profiles for Hexane Extractables and Total Organic Carbon for the two Woodford frac sites.

It is likely that the nature of the organic compounds changes over the flowback period. The data for the initial flowback may be reflective of the compressor oils, diesels and frac chemicals present immediately after a frac operation, while the data for the subsequent flowback may be reflective of more natively present organics (“connate”) or organic species that are more water soluble.

Hardness:

Potential scale-forming ions, such as divalent and trivalent cations, such as Ca, Mg, Al, Ba, Fe, Mn, and Sr, and divalent anions, such as sulfates and carbonates, need to be measured & monitored.

The Total Hardness estimated from the concentrations of the individual potential scale-forming ions and reported in terms of ppm CaCO<sub>3</sub> is shown in Figure 18. We observe that for the Site-1 Days 1-14 flowback, the values climb from an initial ~ 4,000 mg/l CaCO<sub>3</sub> to ~

14,000 mg/l CaCO<sub>3</sub> by Day-14. By contrast, the Day-26 sample from Site-2 shows a significantly lower value of ~ 2,000 mg/l CaCO<sub>3</sub>.

In Figure 19, the Total Hardness is plotted as a function of the TDS in the water samples for the two Woodford frac sites. Interestingly, we observe the Total Hardness showing an almost linear relationship to the TDS. Horn<sup>10</sup> has reported a value of 1163 ppm Total Hardness for a Woodford shale site flowback water containing ~13,800 ppm TDS.

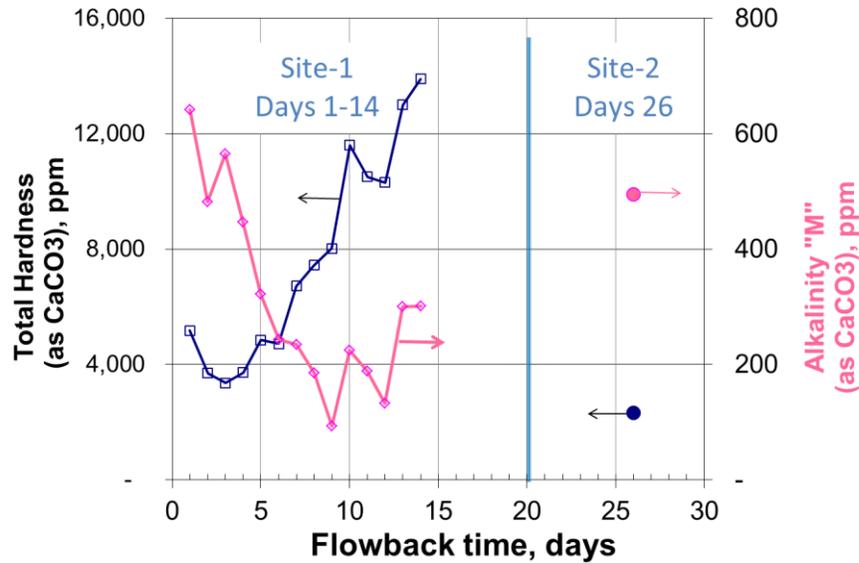


Figure 18. Concentration profiles for Total Hardness and Alkalinity for the two Woodford frac sites.

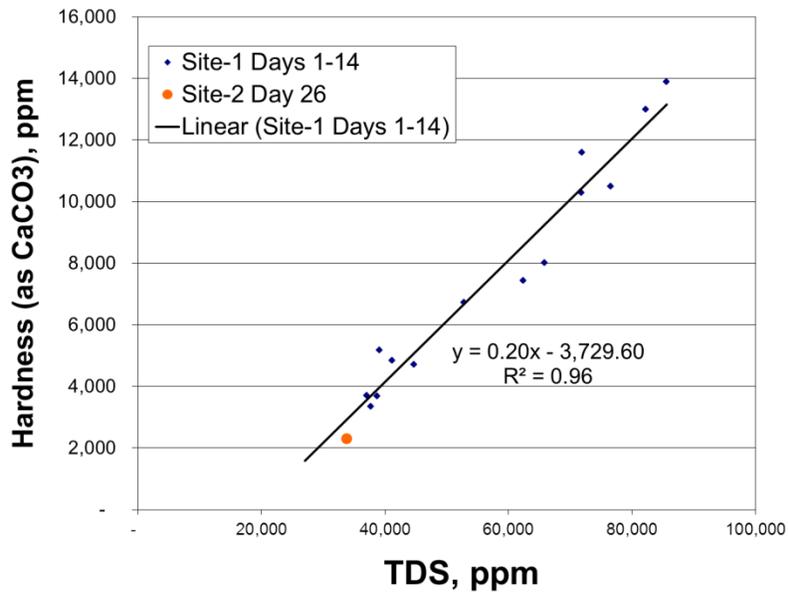


Figure 19. Plot of Total Hardness (mg/l CaCO<sub>3</sub>) vs. Total Dissolved Solids (TDS) for the various frac flowback water samples collected from the two Woodford frac sites.

In Figure 20, the contributions of Ca and Mg to the Total Hardness are further elucidated for the flowback waters from the Woodford shale sites. We observe that for the Site-1 Days 1-14 flowback, nearly 98% of the hardness of the initial flowback is due to Ca & Mg, while this value decreases to ~ 95% for later days. For the Day-26 sample from the Site-2 flowback, Ca & Mg contribute to only 91% of the Total Hardness.

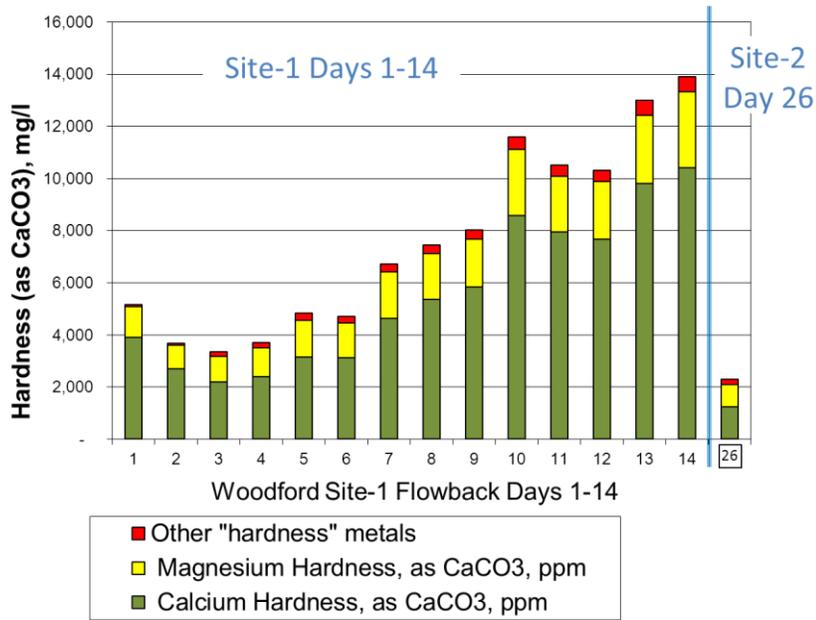
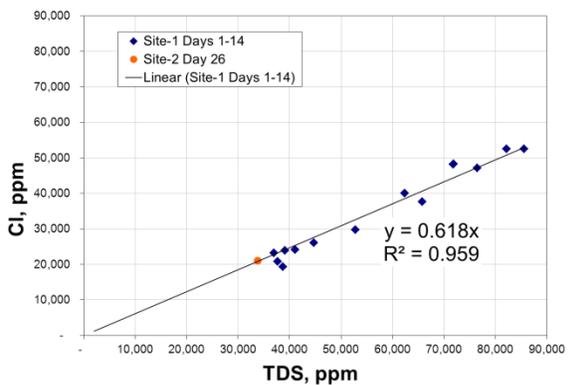


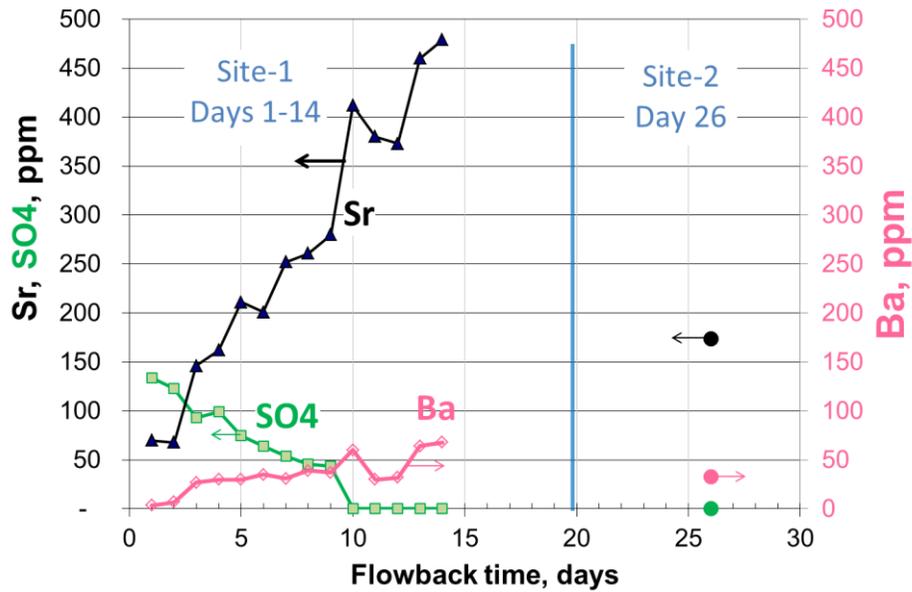
Figure 20. Profiles for the contributions of Calcium, Magnesium and Others (Fe, Sr, Ba) in terms of mg/l CaCO<sub>3</sub> for the two Woodford frac sites.

Interestingly, when the Chloride levels are plotted against the TDS, as shown below, we observe a linear correlation with slope of 0.618, which is remarkably close to the value of the value of 0.608 that we would obtain if we assume that the TDS were entirely due to NaCl (based on the ratio of molecular weights, MCl/MNaCl = 35.5/58.5 = 0.608). However, note that the flowback samples contain varying amounts of the other cationic species besides Na. Such an observation was made earlier with regard to Figure 9 for data from the Marcellus shale.



Barium, Strontium and Sulfates:

Ba as a contaminant is a concern as in many plays the Ba levels are too high for frac reuse due to scaling concerns. Since BaSO<sub>4</sub> has very low solubility, when Ba<sup>++</sup> concentration is high, SO<sub>4</sub><sup>-</sup> concentration is low, and vice-versa. This is apparent in the profiles for Ba, Sr and SO<sub>4</sub> for the two Woodford frac sites seen in Figure 21. We also observe that the Ba concentrations increase from ~3 ppm initially to ~ 68 ppm on Day-14 for the Site-1 Days 1-14 flow-back while the Site-2 Day-26 flowback sample has only ~ 30 mg/l. Horn<sup>10</sup> has reported a value of ~38 mg/l Ba for a Woodford shale site flowback water. By contrast, some areas in the Marcellus shale may have even as high as 6,000 mg/l Ba.



**Figure 21. Concentration profiles for Barium, Strontium and Sulfate for the two Woodford frac sites.**

The Strontium concentration increases from ~ 70 ppm initially to ~ 480 ppm on Day-14 for the Site-1 Days 1-14 flowback while the Site-2 Day-26 flowback sample has only ~ 174 mg/l.

The Sulfate concentrations decrease from ~ 100 mg/l initially to below detection beyond Day-10 for the Site-1 Days 1-14 flowback, while the Site-2 Day-26 flowback sample has negligible concentration.

Iron, Manganese and Boron:

Fe<sup>2+</sup> is a concern as it may oxidize to form Fe<sup>3+</sup>, which may readily form precipitates with various anions. Similarly, Mn may oxidize to form precipitates. The concentration profiles for Fe, Mn and B are plotted in Figure 22 for the two Woodford frac sites.

We observe that the Fe concentration for the Site-1 Days 1-14 flowback is initially ~30 mg/l but decreases to ~ 10 mg/l over the next few days before rising to ~40 mg/l by Day-14. The Site-2 Day-26 flowback water contains ~ 72 mg/l Fe. This is important since the product specifications for frac re-use water require <10 mg/l Fe, as discussed later.

We observe that the Manganese concentration for the Site-1 Days 1-14 flowback is ~ 1 mg/l similar to the Site-2 Day-26 flowback.

We observe that the Boron concentration for the Site-2 Days 1-14 flowback is initially ~10 mg/l and increases to ~18 mg/l by Day-14, while the Site-1 Day-26 flowback water contains ~ 28 mg/l. Boron removal may be a concern if the product water is surface discharged but may not be an issue for frac re-use in slickwater hydrofracturing (however, B levels are tightly controlled in gel-based hydrofracturing).

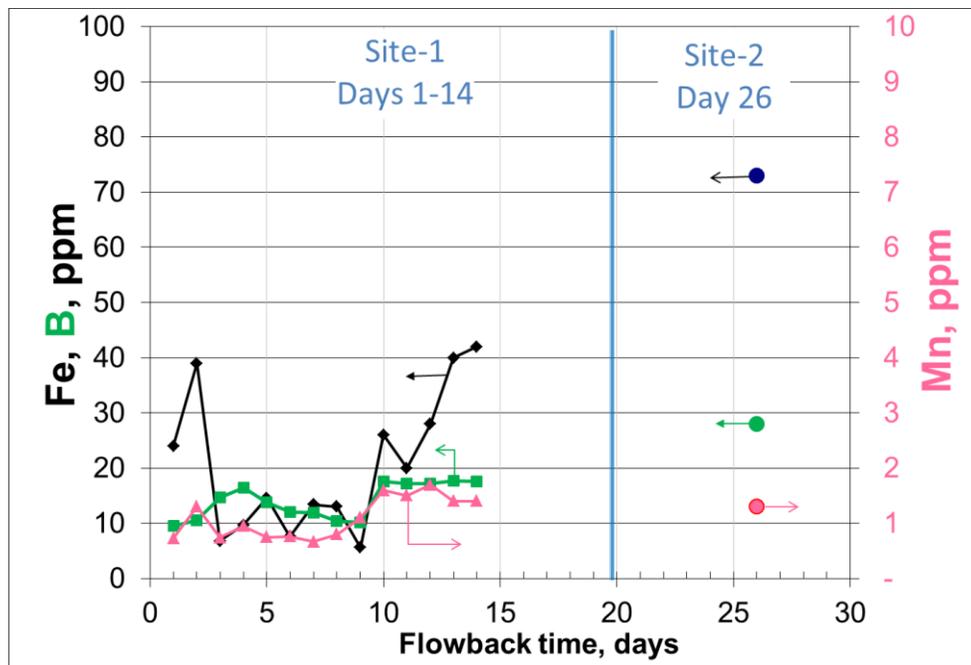


Figure 22. Concentration profiles for Iron, Manganese and Boron for the two Woodford frac sites.

Silica:

Silica may be present in the flowback water either as colloidal silica or reactive silica; the latter is of concern as a potential foulant for desalination membranes. In Figure 23, the concentration profiles for both of these species are plotted as a function of flowback time for the two Woodford frac sites. We observe that there is some variation in both measurements of silica for the Site-1 Days 1-14 flowback with the values between 20 and 70 mg/l: the silica concentration for the Site-1 Days 1-14 flowback is initially ~60 mg/l but decreases to ~ 20 mg/l over the next few days before rising to ~70 mg/l total silica and ~55 mg/l reactive silica by Day-14. The Site-2 Day-26 flowback water contains ~ 120 mg/l total silica and ~60 mg/l reactive sili-

ca. Removal of colloidal silica may occur during removal of suspended solids but removal of reactive silica is important to prevent RO/NF membrane fouling.

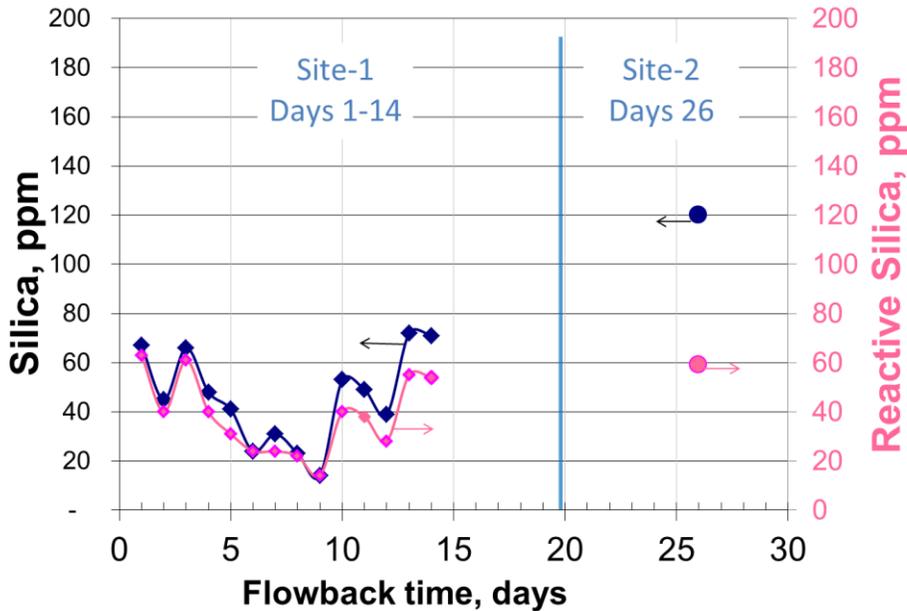


Figure 23. Concentration profiles for Total and Reactive Silica for the two Woodford frac sites.

NORM:

Normally Occurring Radioactive Material (NORM) levels were not measured for these samples. Examination of some of the low-TDS waters from the Woodford shale reveal NORM values in the range from <20 to 500 pCi/L. These are very low compared to values in the Marcellus shale (reported at ~ 10,000 pCi/L). The treatment of NORM containing waters is being specifically addressed by GE Global Research under contract with Research Partnership to Secure Energy for America (RPSEA) (RPSEA 08122-36, principal investigator, Dr. James Silva). The results from that project, when available, will be incorporated into this project.

Composition analysis for the drum samples.

The compositions of the three 55-gal drums obtained from the Woodford shale sites are listed in Table 3. Photographs of vials containing these samples are shown in Figure 24.

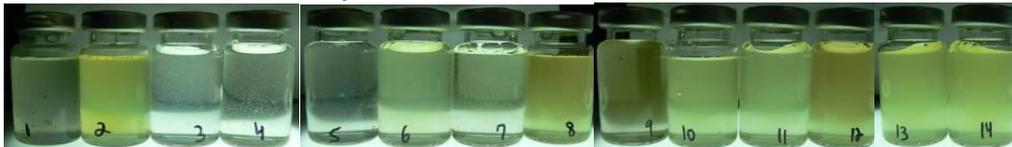
The 33,800 ppm TDS of the Site-2 Day-26 sample was in the desired range for the evaluation of RO-type membrane processes for desalination and was used for membrane fouling studies in Task 4 and 5. Although the TDS values of the water samples obtained from Site-1 were too high for the consideration of RO-type membrane processes for desalination, the samples were useful for the bench-mark evaluation of pretreatment processes for the removal of other undesired components in Task 4.

Table 3. Compositions of the three 55-gal drums obtained from the Woodford shale that were used for bench-mark testing in Tasks 4 and 5.

Components	Site-2 Day 1	Site-2 "Composite"	Site-1 Day 26
Specific Conductance, at 25°C, µmhos	51,100	71,125	54,200
Alkalinity, "M" as CaCO <sub>3</sub> , ppm	641	381	495
Sulfate, as SO <sub>4</sub> , ppm	134	104	35
Chloride, as Cl, ppm	23,900		21,000
Hardness, Total, as CaCO <sub>3</sub> , ppm	5,170	5,838	2,310
Calcium Hardness, as CaCO <sub>3</sub> , ppm	3,910	4,260	1,240
Magnesium Hardness, as CaCO <sub>3</sub> , ppm	1,180	1,348	855
Barium, Total, as Ba, ppm	3	30	33
Strontium, Total, as Sr, ppm	70	186	174
Iron, Total, as Fe, ppm	24	22	73
Sodium, as Na, ppm	14,100	14,600	19,100
Potassium, as K, ppm	301	436	340
Manganese, Total, as Mn, ppm	0.7	1.3	1.3
Phosphate, Total, as PO <sub>4</sub> , ppm	12		12
Silica, Total, as SiO <sub>2</sub> , ppm	67	47	120
Silica, Reactive, as SiO <sub>2</sub> , ppm	63	44	59
Solids, Total Suspended mg/l	841	277	n/a
Solids, Total Dissolved, mg/l	39,100	59,475	33,800
Boron, as B, ppm	10	13	28
Carbon, Total Organic, as C, ppm	187	42	17
Turbidity, NTU	367	143	297
Hexane Extractable Material, mg/l	149	14	

## Frac Flowback Water Sampling

Woodford shale Site1 Days 1-14



Thanks to:  
 • Tom Hook - Woodford samples  
 • Preston Nelms - Fayetteville sample  
 • Mark Wilson & Todd Langford

Woodford shale Site2 Day 26



typical "bottom" of barrel

Figure 24. Photographs of vials containing frac flowback samples from Woodford shale Site-1 Days1-14 and Site-2 Day-26.

### 3.2.11 Specifications for the frac flowback water recovery process

#### 3.2.11.1 Conventional Frac Flowback process

The frac flowback water handling process, although quite complex in terms of the safety and operational logistics, is shown simplified for our purposes in Figure 25. The flowback water is directed to a separator to separate the water from the gas and the solid proppants. The flowback water is stored in interim storage tanks. The water is trucked to water disposal sites.

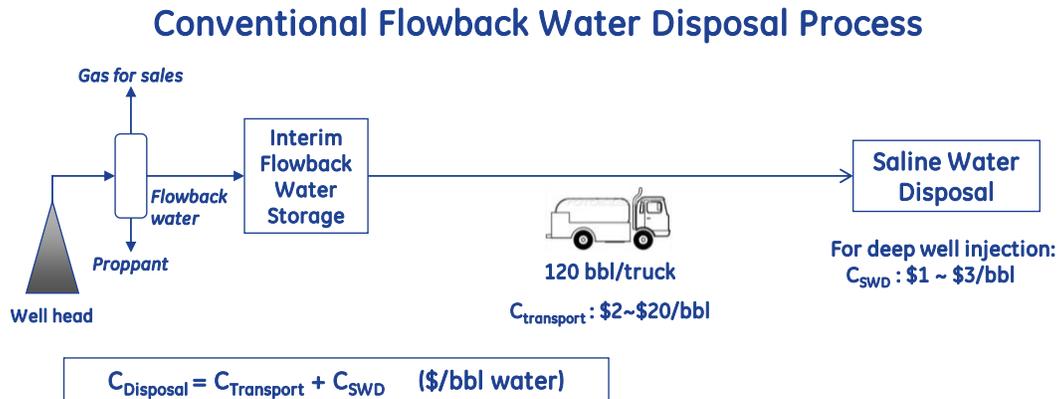


Figure 25. Simplified frac flowback water handling and disposal operation at a shale gas well site.

#### 3.2.11.2 Conventional water disposal

Flowback water may be disposed of by various means including:

- Deep well injection: Disposal in Class II saline water injection sites has been the most common and sometimes the only means of disposal of the high-TDS flowback and produced waters. This has been especially true in the Barnett shale where such disposal sites are available locally and the cost of disposal is relatively cheap at \$1-\$3/bbl. However, such deep well injection sites are few in the Marcellus shale (West Virginia, Pennsylvania, New York), and hence there is a need to transport the flowback waters to sites in Ohio and Indiana. The costs of such long distance hauling by trucks are in the range of \$4- \$19/bbl. An independent operator in the PA area indicated that his disposal costs were ~\$8/bbl. In the Fayetteville shale (Arkansas) it can cost upwards of \$6 per barrel to transport and dispose of water in an independently owned disposal well<sup>3</sup>. For the Woodford shale (Oklahoma), the trucking costs are estimated at \$3.71/bbl and disposal between \$1-2/bbl<sup>10</sup>.
- Surface water discharge: Until recently, this mode of disposal was used in the Marcellus shale in the PA area. PA DEP 25 regulations enacted in August 2010 limit surface discharge from Oil & Gas operations to less than 500 ppm TDS (among other specific constituents such as Chlorides, Sulfates, Barium and Strontium).
- Land farm use: This was used until recently in the Fayetteville shale in Arkansas, but there are restrictions to such use<sup>3</sup>. Waters cannot be land applied when the ground is saturated, frozen, or if precipitation is imminent. In order for water to be applied to the surface under land application permits, it must have a chloride concentration of

less than 5,000 parts per million (ppm) and comply with a Sodium Adsorption Ratio (SAR) specifications. If chloride content is less than 1,500 ppm, water can also be utilized on roads for dust suppression. If chloride concentrations exceed 5,000 ppm, disposal in approved disposal wells is required.

### 3.2.11.3 Frac Flowback Recovery Process

A conceptual process for recovering all or part of the flowback water for re-use in hydrofracturing operations is shown in Figure 26. The flowback water recovery process (FWRP) is preferably located physically close to the well operations to minimize water hauling costs. It includes a mobile unit equipped with the necessary treatment operations to provide a “product” water that meets specifications for re-use in hydrofracturing. Only a portion of the flowback water may be recovered as product, while the rest may have to be disposed of either in conventional saline water disposal Class II wells or via further recovery by methods suitable for desalination of high-TDS waters (> 70,000ppm), such as thermal processes.

### Flowback Water Recovery Process for Frac Re-use

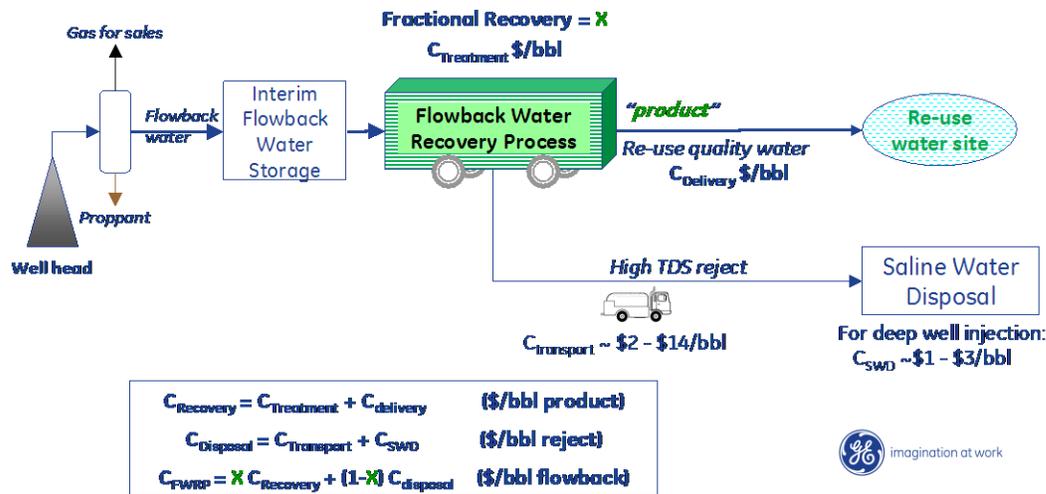


Figure 26. Conceptual Flowback Water Recovery Process (FWRP) for re-use in hydrofracturing. The overall cost will depend on the extent of water recovery, x, in the FWRP.

### 3.2.12 Technical specifications for recovery for frac re-use

#### 1. Product composition:

The contaminants of interest in the frac flowback water for mitigation and their impact on water re-use for hydrofracturing are shown in Figure 27.

## Frac Flowback: Key Contaminants



**Figure 27. Key contaminants in frac flowback water and their impact on re-use in hydrofracturing.**

Opinions vary widely on the water quality that may be used for hydrofracturing. For instance, most of the operators currently insist on using very low-TDS source water to avoid scaling issues in the downhole piping. Some well operators, such as Range Resources, have reported success in using up to 26,000 ppm Chlorides in the Marcellus shale<sup>16</sup>. In fact, Range Resources and Chesapeake reported at the 2010 GWPC Conference, Pittsburgh, PA that they presently re-use ~100% of early flowback water in the Marcellus shale by blending with fresh water (TDS<500 ppm) in subsequent hydrofracturing operations. Some experts feel that water salinity equivalent to seawater, namely ~ 35,000 ppm TDS may be usable for hydrofracturing<sup>5</sup>. Some operators are reportedly even considering the re-use of waters with salinity as high as 120,000 ppm TDS with low hardness and scale-causing contaminants<sup>17</sup>, but we consider these to be highly speculative at the present moment as these may be applicable to specific situations where blending with a majority of very low-TDS source water may be anticipated before frac use.

To develop specifications for frac re-use water, we evaluated the limited information available in literature and spoke to frac operators. The data provided by Range Resources<sup>4</sup> gives one benchmark for re-use specifications. This is reproduced in Figure 28 and provides a good understanding of a practical application. Apparently, the frac flowback waters from a Marcellus shale well site were blended with fresh water to create a frac fluid with the reported characteristics, which was successfully used for hydrofracturing at another site.

Parameter	Conventional Limits	Blended Marcellus Water	Considerations
pH	6.0 to 8.0	8.1	Fluid Stability, Scaling
Chlorides	<20,000 mg/L	26,000 mg/L	Fluid Stability
Iron	<20 mg/L	14.5 mg/L	Fluid Stability
Ca, Mg, Ba, SO <sub>4</sub> , CO <sub>3</sub> , ...	f(P,T,pH) (+/- 350 mg/L)	Ca – 4,200 mg/L, Mg – 488 mg/L, Ba – 39 mg/L, SO <sub>4</sub> – 124 mg/L	Scaling
Bacteria Count	<100/100 mL	1 million/100 mL	Bacteria Growth
Suspended Solids	<50 mg/L	1,500 mg/L	Skin
Oil & Soluble Organics	<25 mg/L	4.6 mg/L	Fluid Stability

**Figure 28. Summary of chemical characteristics of the waters used in conventional and blended Marcellus waters used for hydrofracturing by the Range Resources Company<sup>4</sup>.**

A specification for re-use frac water apparently developed with data supplied by Halliburton and XTO Energy are provided in Table 4.

**Table 4. The following specifications for re-use frac water in the Marcellus shale were apparently developed<sup>18</sup> with data supplied by Halliburton and XTO Energy**

Parameter	Range
maximum scale formers*	2,500 mg/l as CaCO <sub>3</sub>
maximum dissolved solids	50,000 mg/l
maximum iron	3.5 mg/l
maximum calcium	250 mg/l
pH range	6.5 to 7.5

\* scale formers are generally considered to be aluminum, barium, calcium, iron, manganese, and strontium

Moreover, the methods used for hydrofracturing are being continuously updated as the industry is trying to maximize gas recovery while minimizing energy and especially, fresh water usage. For example, current research on new slicking agents (friction reducers) may allow the use of higher salinity in the feed water compared to present operations. Regulations are being considered by various state and federal agencies on the disclosure of water chemistry used for hydrofracturing, discharge of flowback water, and the re-use of flowback water for hydrofracturing. Until the frac industry has honed in on their requirements, there will be uncertainty on the specifications for the treated water and discharge water. This affects the determination of how much of the flowback water would be treatable, the choices of technology options applicable and the overall system cost. *The conclusion from our survey was that the specifications for acceptable re-use are subject to change in the short-term.*

Based on the feedback from hydrofracturing operators, it was realized that the team needed to update the product water scope from the one product with 20,000 ppm TDS originally proposed to potentially four alternative products with varying levels of purification:

1. **Product-1:** Clarified only (removal of suspended matter, free oil & grease, Fe, and microbiological contaminants),
2. **Product-2:** Softened and Clarified (removal of hardness ions, namely Ba, Sr, Ca, Mg besides the purity specs for Product-1),
3. **Product-3:** Partially desalinated to < 20,000 ppm TDS (besides the purity specs for Product-2), and
4. **Product-4:** Substantially desalinated to < 500ppm TDS (besides the purity specs for Product-2).

These product options and the associated target contaminants for removal are shown in Figure 29.

## Frac Flowback Recovery: Product Options

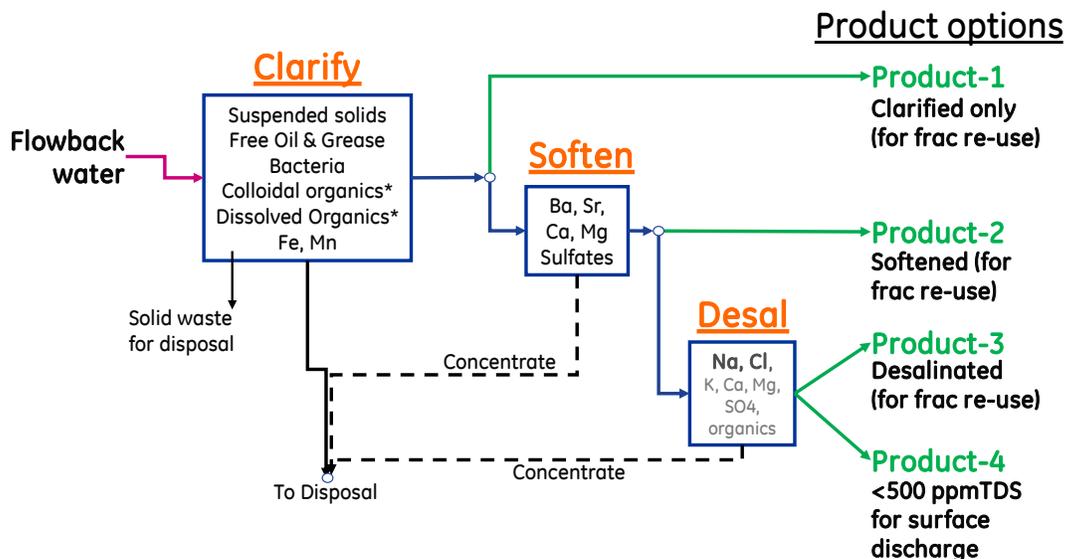


Figure 29. . Product Options for frac flowback water recovery. The target contaminants are listed for each process step in the respective boxes. The target contaminants to be removed in each process step are indicated inside the boxes.

The specifications for the products under consideration are shown in Figure 30. It should be noted that as the shale gas industry is continually evolving in terms of the water quality used for hydrofracturing, the specifications are based on currently best available information from operators and published literature. The first three product waters would be suitable for re-use in hydrofracturing while Product-4 would also be suitable for surface discharge. It should be noted that the product quality requirements increase as we consider Product-1 through Product-4, both in terms of the number of target contaminants as well as the extent of their removal. For example, dissolved organic contaminants at levels < 50 ppm may not be as much of an issue with Product-1 and Product-2, namely Clarified-only and Softened-only, respectively; however, these contaminants at levels >10 ppm may be foulants for the desalination membranes that would be used to produce Product-3 and Product-4.

## Requirements for the "product" waters

Parameter	Units	Conventional "fresh" source water before additive blending	Conventional frac fluid after additive blending	* "Clarified product" for re-use	* "Softened product" for re-use	* "Desal water" product for frac re-use	* "Desal water" product for agricultural discharge
Total Dissolved Solids	mg/L	<500	<1000	NR	NR	<20,000	<500
Total alkalinity	mg/L	~ 50	~50	<600	<600	<600	~ 50
Hardness as CaCO3	mg/L	<150	<150	NR	<2000	<2000	See SAR
Total suspended solids	mg/L	<2 ~ 10	<50	<50	<50	<50	<2 ~ 10
Turbidity	NTU	<4	<250	<100	<100	<100	<4
Chloride	mg/L	<50	<100	NR	NR	<12,500	<50
Iron	mg/L	<4	<10	<10	<10	<10	<4
Oil & soluble organics	mg/L	<10	<400	<50	<50	<50	<29
Sulfate	mg/L	<25	<25	<125	<25	<25	<25
Total Phosphorus	mg/L	~0.1	0.1 ~ 5	NR	NR	NR	<5
Bacteria Count	#/100mL	<100	<100	<100	<100	<100	<100
pH		6.7 - 7.4	5.2 - 8.9	6.5 - 8.5	6.5 - 8.5	6.5 - 8.5	6.7 - 7.4
SAR				NR	NR	NR	<12
Temperature	C			NR	NR	NR	ambient

\* Best available specifications from few operators and published literature. Actual values may vary depending on shale formation, local regulations and operator preferences.

**Figure 30. Specifications for the various Product Options described in Figure 29.**

Note that due to addition of the various chemicals for friction reduction, etc. (see Appendix for details), there is a net increase in the TDS and other components in the frac fluid relative to the source water, as seen in Figure 30 for the compositions of the frac fluid before and after additives blending for a conventional "fresh" water source. Also, the specifications for Product-3 appear to be roughly half of the Chlorides and TDS reported by Range Resources in Figure 28. We felt that it was prudent to take a conservative approach.

### 2. Extent of product recovery

The extent of recovery of the product water (fit for frac re-use),  $x$ , is defined as:

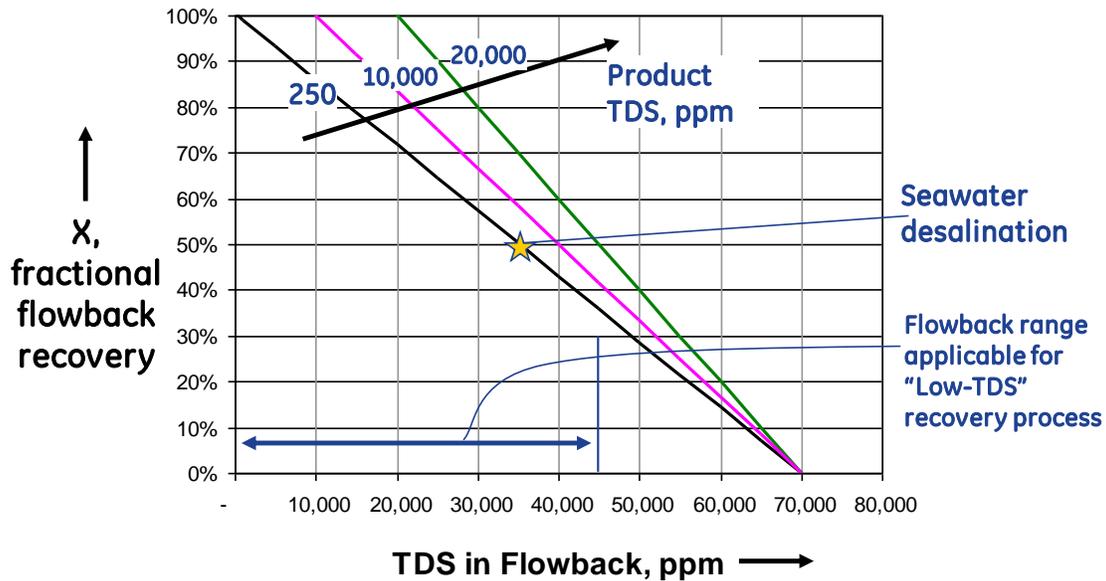
$$x = \frac{\text{Volume recovered water}}{\text{Volume flowback water}}$$

For Product-1 and Product-2 in Figure 29 that involve only processes such as filters, clarifiers, sorbents, and precipitation equipment, the water recovery is typically >90% or higher depending on the efficiency of the sludge handling methods employed.

However, the extent of product permeate recovery in membrane desalination processes is limited by the feed water composition (including salts, hardness ions, silica, organics, etc.), the pressure limitations of the pumping equipment used and the membrane area available. As water permeates through the selective membrane inside the permeator module, the concentration of salts and other non-permeable components, such as silica, organics, etc., increase in the retentate. This results in the need for a greater pressure drop across the membrane for reasonable permeate production rates, and also increases the potential for precipitation of insoluble salts, such as CaCO<sub>3</sub>, CaSO<sub>4</sub>, BaSO<sub>4</sub>, SrSO<sub>4</sub>, etc. and fouling of the membrane by reactive silica and other contaminants. Typically, for economically viable sea water desalination, the upper limit on the concentration of the retentate in RO processes is about 70,000

ppm – the actual value will depend on the concentrations of the other ions, silica and other components.

In Figure 31, the extent of recovery,  $x$ , is plotted as a function of the flowback TDS concentration for different values of the permeate product TDS concentrations, namely 250 ppm, 10,000 ppm and 20,000 ppm. The value of 250 ppm TDS corresponds to a very low-TDS product that is suitable for potable water or surface discharge (Product-4), and the value of 20,000 ppm TDS corresponds to our proposed “frac re-use” (Product-3) specifications shown in Figures 29 & 30. The condition for typical seawater desalination to produce potable water (<250 ppm TDS) is also shown in Figure 31.



**Figure 31. Plot of extent of product recovery,  $x$  as a function of the flowback water concentration and desired permeate product water concentrations when retentate concentration is limited to 70,000 ppm TDS.**

The applicable range of flowback water composition for “Low-TDS” recovery processes is expected to be in the range of 15,000 to 45,000 ppm TDS depending on the shale play under consideration (see Table 2 for expected TDS ranges for different shales). **For flowback water concentrations in the range of 30,000 to 45,000 ppm, the expected extents of recoveries are 50-80% for Product-3 (20,000 ppm TDS product) and 35-55% for Product-4 (500ppm TDS product).**

### 3. Cost criteria:

#### *Value Assessment of Flowback Water Recovery Process*

The value of the Flowback Water Recovery Process (FWRP) would depend on the specifics of the shale site. The factors to consider are (a) the salinity and other contaminants in the flowback water that would limit the recovery ( $x$ ), (b) the cost of conventional disposal options, (c)

any regulations (penalties) related to disposal of the flowback waters or use (benefits/incentives) of the product water for frac re-use, (d) the availability (or lack) of water for frac use, and (e) the cost and logistics of the infrastructure available to bring in a mobile unit at the frac flowback site.

The acceptable cost target of the recovery process would consequently be dependent on the specifics of the shale site under consideration. Of course, the preferred option is the “cheapest” process that meets the technical specifications at the “highest” recovery.

When we consider the cost of a FWRP, we need to consider the following:

- Cost of recovery process to produce a product fit for frac re-use.
- Delivery of the product to the re-use site
- Value benefit of the fresh water avoided during the subsequent frac operation.
- Disposal of the unrecovered product via deep well saline water injection or some other recovery method (e.g. thermal recovery) including transportation.

These are represented below:

$$C_{FWRP} = C_{Recovery} + C_{Concentrate\ disposal} \quad (\$/bbl\ feed) \quad (1)$$

$$C_{Recovery} = C_{Treatment} + C_{Product\ Delivery} - (C_{Fresh\ Water} + C_{Penalties\_Avoid}) \quad (\$/bbl\ product) \quad (2)$$

where the cost for the product recovery  $C_{Recovery}$  includes the cost of the treatment processes and the cost for delivery of the product water to the re-use site. Additionally, credits could be taken for the value of the fresh water avoided during the next fracturing job, and any avoidance of penalties from existing or pending regulations.

The volume and cost of water being withdrawn, and consequently not available for public consumption, is a significant public perception issue, especially during water-constrained situations (drought, etc.). But in most shale plays when water availability is not a concern, fresh water from river water and municipalities typically costs ~ \$0.05/bbl plus delivery, which may result in a net cost of ~\$0.22/bbl. This cost is small compared to typical saline water Class II disposal costs of \$1-3/bbl. The value of the penalties avoided,  $C_{Penalties\_Avoid}$  is unknown at the moment. Hence, although inclusion of  $C_{Fresh\ Water}$  and  $C_{Penalties\_Avoid}$  offers a more economically attractive condition, a more conservative approach would be to ignore them, as in eqn. (3):

$$C_{Recovery} \cong C_{Treatment} + C_{Product\_Delivery} \quad (\$/bbl\ product) \quad (3)$$

The cost of delivery,  $C_{Product\_Delivery}$  will again vary depending on the distance between the re-use site and flowback site, and the mode of product water transfer. The cheapest option will be to pump into a local pond dedicated to hold this product until re-use. The most expensive

option will be trucking over long distances. A reasonable estimate would be  $C_{\text{Product\_Delivery}} < \$0.1\sim 0.5/\text{bbl}$ .

For the Flowback Water Recovery Process to be economically attractive, the minimum requirement is:

$$C_{\text{FWRP}} < C_{\text{Conventional Disposal}}$$

From our earlier discussions, we noted that the typical conventional disposal costs, including transportation, could vary depending on the individual shale plays and the availability of disposal sites. These values range from as low as \$2-\$4/bbl in Barnett to as high as \$4-\$19/bbl in Marcellus, while it is \$6/bbl in Fayetteville<sup>3</sup> and \$3.71/bbl for transportation and ~\$1-2/bbl for disposal in Woodford<sup>10</sup>. (Although, interestingly, during the Pennsylvania Chap 95 regulation analysis review, it was reported that even at costs anticipated for proper treatment and disposal at as high as ~\$10/bbl, the annual costs would comprise a mere 0.4% of the estimated annual revenue<sup>19</sup>).

From these values and feedback from a few well operators, as well as paring down the contributions of product handling & delivery costs and rig operating labor, the treatment cost criterion for this project was set as:

$$C_{\text{Treatment}} < \$2/\text{bbl feed}$$

Where  $C_{\text{Treatment}} = C_{\text{Setup}} + C_{\text{Process}}$

$C_{\text{Setup}}$ : Cost of mobile rig transportation and setup at the frac site.

$C_{\text{Process}}$ : Cost associated with the capital and operating expenses related to the process steps including process equipment, chemicals, waste disposal and maintenance.

This is the treatment cost on-site and does not include the cost of product- and concentrate-disposal. The labor costs associated with setting up the mobile rig are included in  $C_{\text{Setup}}$  and thus in the  $C_{\text{Treatment}}$  value. However, the rig operating labor for treating flowback water has not been included since these costs may be accounted differently by different producers as the rig may be run by operators handling multiple responsibilities at the frac site.

### 3.2.13 Summary of the verification of success criteria

The verification of success criteria are summarized in Figure 32.

## Verification of success criteria:

### ☐ Performance:

### Requirements for the "product" waters

Parameter	Units	Conventional "fresh" source water before additive blending	Conventional frac fluid after additive blending	*Clarified product" for re-use	* "Softened product" for re-use	* "Desal water" product for frac re-use	*"Desal water" product for agricultural discharge
Total Dissolved Solids	mg/L	<500	<1000	NR	NR	<20,000	<500
Total alkalinity	mg/L	~ 50	~50	<600	<600	<600	~ 50
Hardness as CaCO3	mg/L	<150	<150	NR	<2000	<2000	See SAR
Total suspended solids	mg/L	<2 - 10	<50	<50	<50	<50	<2 - 10
Turbidity	NTU	<4	<250	<100	<100	<100	<4
Chloride	mg/L	<50	<100	NR	NR	<12,500	<50
Iron	mg/L	<4	<10	<10	<10	<10	<4
Oil & soluble organics	mg/L	<10	<400	<50	<50	<50	<29
Sulfate	mg/L	<25	<25	<125	<25	<25	<25
Total Phosphorus	mg/L	~0.1	0.1 - 5	NR	NR	NR	<5
Bacteria Count	#/100mL	<100	<100	<100	<100	<100	<100
pH		6.7 - 7.4	5.2 - 8.9	6.5 - 8.5	6.5 - 8.5	6.5 - 8.5	6.7 - 7.4
SAR				NR	NR	NR	<12
Temperature	C			NR	NR	NR	ambient

### ☐ Product recovery:

>95%    >90%    >50%    >40%

### ☐ Cost of FWRP < Cost of Conventional Disposal

### ☐ Treatment cost <\$2/bbl feed

### ☐ Mobile rig configuration feasibility

\* Best available specifications from few operators and published literature. Actual values may vary depending on shale formation, local regulations and operator preferences.

Figure 32. Verification of success criteria for the Low-TDS frac flowback recovery process

### **3.3 Task 3: Define conceptual process alternatives for frac water recovery for re-use**

The specific objective was to:

- Evaluate possible frac water recovery flow schemes and obtain preliminary costs.

The key activities were to:

- Identify potential treatment technologies for the various contaminants identified in Task 2.
- Generate preliminary process schemes with these various technology options and evaluate potential feasibility and risks to meet the technical product requirements, cost targets and mobility requirements.

We reviewed available technology options to remove the various contaminants of interest in frac flowback water. Additionally, we, at GEGR, worked closely with various groups within GE Water & Process Technologies (GEWPT) to leverage their knowledge in treating various industrial waste waters. Specifically, GEWPT Water Chemicals division offers a wide product portfolio of chemicals used for membrane-water pretreatment and corrosion prevention, GEWPT Membranes division offers a wide product portfolio on microfiltration, ultrafiltration, nanofiltration, reverse osmosis, and membrane bioreactors for treating various municipal and industrial waste waters. GE WPT Mobile Services offers the world's largest fleet of mobile water treatment systems, providing rapid response for a full range of reverse osmosis, filtration, demineralization, softening, and deoxygenation treatment on demand.

#### **3.3.1 Frac Flowback Water Recovery Process Options**

A conceptual Frac Flowback Recovery Process (FWRP) scheme for treating the frac flowback water to provide product water fit for frac re-use is shown in Figure 33.

# Frac Flowback Recovery Process

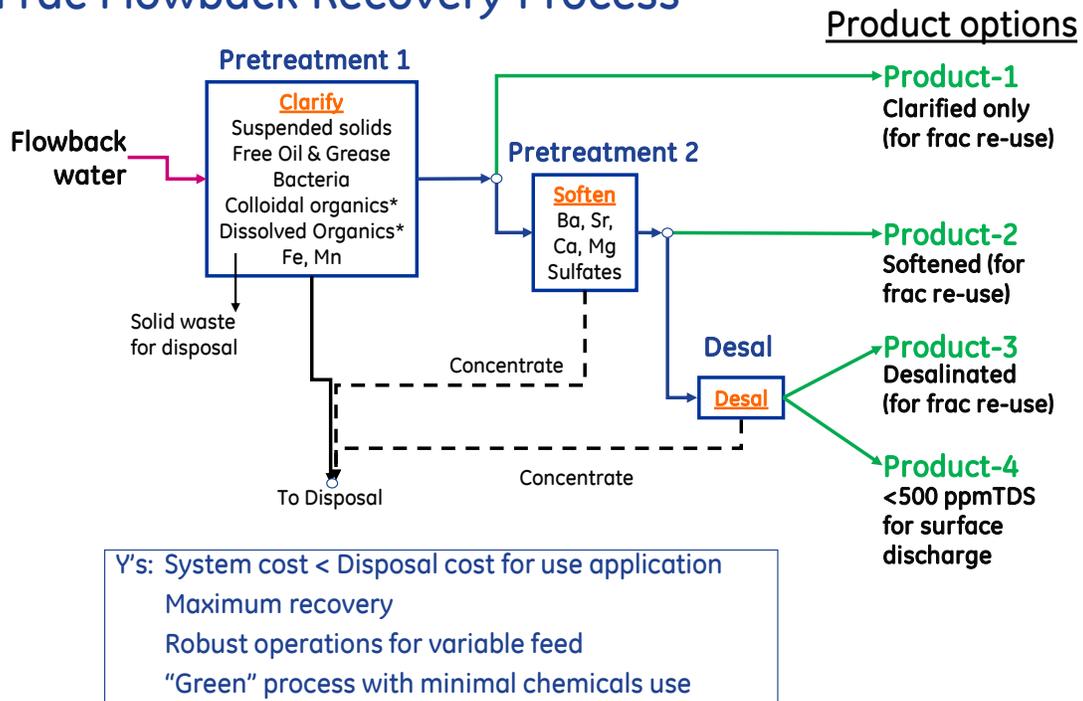


Figure 33. Conceptual representation of a frac flowback recovery process to treat the frac flowback waters to provide the product options in Figure 30. The target contaminants to be removed in each process step are indicated inside the boxes.

The flowback water is first treated to remove the various contaminants shown in the Pretreatment-1 box in Figure 33. The key contaminants to be removed are suspended solids, free oil & grease, bacteria, colloidal organic and inorganic material. Dissolved ions are not removed. The outputs from this process are: (a) a clarified "product" stream that will meet the Product-1 requirements specified in Figure 30, and (b) a small solids-rich waste stream produced from the precipitation and filtration steps for disposal.

For Product-2, the output from Pretreatment-1 may be further treated to remove hardness-causing ions, mainly divalent and trivalent ions, in the step shown as Pretreatment-2 in Figure 33. It is possible, as shown later, to combine the processes in the Pretreatment-1 and -2 steps. The outputs from this process are: (a) a softened "product" stream that will meet the Product-2 requirements specified in Figure 30, and (b) a solids-rich waste stream that needs to be disposed of, preferably as a non-hazardous waste disposed of in a land-fill, or a liquid waste stream that is concentrated in the divalent and trivalent ions that is disposed of in an underground saline water injection facility. The solids-rich waste stream would be generated when precipitation methods such as "lime softening" are used, followed by settling and filtration. A liquid-rich waste stream would be generated when a nanofiltration membrane process that selectively rejects di- and tri-valent ions is employed. The extent of water recovery is definitely higher for the solids-precipitation method but it requires handling of solids.

To meet the Product-3 and Product-4 requirements, the output from Pretreatment 2 would require the use of desalination membranes that selectively exclude the permeation of monovalent ions, such as Na, K, and Cl besides any residual divalent and trivalent ions. The extent of salt removal is influenced by the choice of desalination membranes employed. The extent of removal could be least when nanofiltration (NF) membranes that remove the divalents and some of the monovalents are employed and most when high-selectivity reverse osmosis (RO) membranes are employed. The NF membranes have the highest permeate flux and would require the lowest membrane area and lowest operating pressure (~100 psig range), while the high-selectivity RO membranes typically have the lowest flux and would require the largest membrane area and highest operating pressure (800-1200 psig), and thus the highest electrical power consumption (kW/m<sup>3</sup> of permeate). Membranes with intermediate ranges of flux and selectivity may also be considered for an optimal flux/area/power requirement for the desired product TDS quality.

The retentate or concentrate stream from the membrane desalination process would be sent to disposal in deep well injection wells, or as feed to thermal desalination systems that can recover more useful water for reuse and further concentrate the saline stream to reduce the volumes for deep well injection. An ideal situation would be in a zero liquids discharge (ZLD) facility wherein all the water is recovered and the residue is a valuable by-product salt useful as an industrial raw material or as road-salt.

### **3.3.2 Key contaminants in frac flowback of concern for reuse**

The contaminants in the frac flowback water were discussed in Section 3.2.10.3 and their impact on water reuse for hydrofracturing were illustrated in Figure 27. The salient aspects of these contaminants for evaluating process technology options for cleanup are described below:

- **Particulates:** These could be precipitated solids, sand and silt, carbonates, clays, proppant, corrosion products, and other solids derived from the producing formation and from well bore operations. Quantities can range from insignificant amounts to high enough to yield a solids slurry. In theory, these should be amenable to removal via filtration or other mechanical means.
- **Suspended solids:** These are finer particulates of inorganic, metallic or organic materials. They can also be colloidal in nature. Reported values are typically ~ 200 ppm but could be much higher depending on the particular operating conditions of the flowback. There could be significant variability in the values during the flowback.
- **Free oil and grease (FOG):** These could be from the oils and diesels from compressors and other drilling equipment or native from the producing formation. There is a lot of fluctuation in the reported values even in the same shale. There could be significant variability in the values during the flowback.

- Dissolved Organics: These could be small amounts of low molecular weight hydrocarbons, polymers used as friction reducers (see Appendix), or other organics from the formation. Reported values range from 10 – 150 ppm.
- Volatile Organics: Some of the dissolved and undissolved organics could be considered as volatile under normal operating conditions and as such may present concerns with emissions or fire/explosion hazards if the concentrations are too high. Condensates present in the shale gas that contaminate the flowback water, especially benzene, toluene and xylenes, need to be explored as they are of public concern. Most literature values indicate <10 ppm for such compounds.
- Hardness: These include divalent ions, with the ions of most concern being Ca and Mg. The concentrations of these ions are high in certain shales, such as Marcellus while low in shales such as Woodford and Fayetteville. They could range from ~100 ppm to 10,000 ppm depending on the shale and vary as a function of flowback time (typically increase almost linearly with TDS).
- Barium: Ba as a contaminant is a concern as in many plays the Ba levels are very high. Since BaSO<sub>4</sub> has very low solubility, when Ba<sup>++</sup> concentration is high, SO<sub>4</sub><sup>-</sup> concentration is low, and vice-versa (see Figure 11 for the Haynesville shale data). Reported Ba values range from <100 ppm in Woodford to as high as 6,000 ppm in certain areas of Marcellus. Even in Marcellus, there is significant variation as one travels from WV via PA to NY.
- Strontium: Reported values range from <50 ppm in Woodford to >2,000 ppm in Marcellus.
- Iron: Reported values range from 20-200 ppm. Fe<sup>++</sup> is a concern as it may oxidize and form precipitates with various anions.
- Silica: Reported values range from 10 – 120 ppm. This could be colloidal silica or reactive silica; the latter is of concern as a potential foulant for desalination membranes.
- NORM: NORM originates in geological formations and can be brought to the surface with the flowback water. The NORM values for some of the low-TDS waters from the Woodford shale appear to range from <20 to 500 pCi/L. These low values do not pose any concerns for treated water or any waste residues produced during recovery of the saline waters considered in this project.

### 3.3.3 Considerations for evaluating technology & process options

A review of available technology options to remove the various contaminants of interest in frac flowback water was conducted. Process flow schemes with these technology options were created. The technology options were rated for the following:

- Technical Performance: Will the technology option remove the contaminant to the desired specification? Can it be integrated with the other process technologies to yield a technically workable process solution?
- Cost Performance: Will the technology be cost-effective? Will the overall process cost incorporating this technology be cost-effective?

- Mobility Performance: Does this technology have a low enough footprint that makes it amenable to incorporation into a mobile rig? Will the overall process using this technology be usable in a mobile rig?

The following rating scale was used:

- Green: The risks are low with this technology option for this contaminant. Also, overall process integration with this technology carries low risks
- Yellow: There are some low-med level risks with this technology option that would need to be retired either using pretreatment or post-treatment. For example, polyamide membranes typically used for desalination will get fouled at high concentrations of reactive silica or precipitating salts, such as  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ , etc. Therefore, there is need to pre-treat the feed to this membrane unit to remove the potential foulants or add anti-scaling agents.
- Red: The technology option has some substantial risks that need to be retired by either pretreatment or post-treatment.

The results of the analysis are shown in Figure 34. The conclusions from the analyses are discussed in the next section.

Technology	Brief description		TSS	TDS (monvalent)	Ca, Mg	Silica	Iron 2+	O&G	dissolved organics	Ba
Oil water separator	Coalescence of oil and removal through flotation	Performance Risks Cost risk Mobility	small particles							
Hydrocyclone	Utilized centrifugal force to separate solids and oils from water	Performance Risks Cost risk Mobility	small particles							
Lime softening	Addition of lime and soda ash to water to achieve hardness removal	Performance Risks Cost risk Mobility				dissolved Si				
Chemical Precipitation	Coagulant addition to develop floc, removing TSS, O&G, and di-/trivalent ions	Performance Risks Cost risk Mobility				dissolved Si				via sulfate
Electrocoagulation	Uses electricity to dissolve an iron or aluminum electrode, and developing floc.	Performance Risks Cost risk Mobility			scale on electrode	dissolved Si			uncertain removal	
Dissolved air flotation	Clarification of water by contact with minute bubbles, floating air/floc mass to surface	Performance Risks Cost risk Mobility	small particles							
Aeration and sedimentation	Aeration to oxidize reduced species to less soluble state.	Performance Risks Cost risk Mobility								
Biological Treatment	Process where microbes degrade organics.	Performance Risks Cost risk Mobility						high levels		
Sand or multi-media filtration	Vessel filled with sand or other granular media to remove TSS or colloids from water passed through it	Performance Risks Cost risk Mobility						smaller droplets		
Bag filters	A dead-end filter made of mesh material of specific micron size to remove TSS.	Performance Risks Cost risk Mobility	fast loading							
Ion exchange	The reversible exchange of ions between the liquid and a solid resin	Performance Risks Cost risk Mobility			fouling risk	Si specific resin				
Walnut shell filter	Filter made from crushed walnut shells for O&G removal	Performance Risks Cost risk Mobility	small particles					not for high conc		
activated carbon	A highly adsorbent form of carbon used to remove dissolved organic matter from water	Performance Risks Cost risk Mobility						foul at high conc		
Organoclay	Bentonite clay modified with quaternary amines, used as an adsorbent for O&G	Performance Risks Cost risk Mobility								
Fentons	Advanced oxidation using Fe and H2O2 to produce hydroxyl radicals to degrade organics.	Performance Risks Cost risk Mobility						kinetics, chemicals		
Ozone	A strong oxidizing agent able to degrade organics.	Performance Risks Cost risk Mobility						kinetics, chemicals	foaming	
Chlorination	A strong oxidizing agent, although not as strong as ozone.	Performance Risks Cost risk Mobility								
Potassium permanganate	Used for oxidation of iron and manganese	Performance Risks Cost risk Mobility					dosing, filter fouling			
Microfiltration	Low pressure membrane filtration process for removing TSS and colloids > ~0.1um (cutoff varies by membrane)	Performance Risks Cost risk Mobility	small particles							
Ultrafiltration	Low pressure membrane filtration process for removing TSS and colloids >~20nm (cutoff varies by membrane)	Performance Risks Cost risk Mobility								
Nanofiltration	Medium pressure membrane process for removing di- and tri-valent ions and species > ~1nm	Performance Risks Cost risk Mobility			fouling*	fouling*	fouling*			fouling*
Reverse Osmosis	Method for separating water from dissolved salts by passing feedwater through a semipermeable membrane at a pressure greater than the osmotic pressure.	Performance Risks Cost risk Mobility			fouling*	fouling*	fouling*			fouling*
Electrodialysis	Separation of ionic components using semipermeable ion-selective membranes operating in an electric field	Performance Risks Cost risk Mobility			fouling*	fouling*				

Figure 34. Technology options evaluated in the preliminary screening in Task 3 for removal of the various contaminants in frac flowback water. Each of the options was evaluated for potential risks with performance individually and upon integration into a process. Costs risks were based on overall process satisfying the \$2/bbl feed treatment cost criterion. Mobility risks were for incorporating the technology and the integrated process

## 3.4 Task 4: Evaluate key Pretreatment and Membrane Processes in bench-scale experiments

### 3.4.1 Objectives and Approach

The specific objectives were:

- Evaluate pretreatment methods and RO/NF membranes for treating frac flowback water via bench-scale experiments
- Make a go/no-go decision based on whether pretreatment methods for effective removal of the contaminants are technically feasible and cost-effective.

### 3.4.2 Bench-scale experimental approach

The extent of removal of contaminants and water recovery will depend on the flowback concentration and the desired product concentrations for the Product options 1-4 described in Figure 30. The various mechanical, chemical and membrane technologies that were identified to be 'Green' in Task 3 were evaluated via bench-scale laboratory experiments. The experiments were conducted initially with simulated frac water (pure water mixed with known concentrations of one or more target contaminants) and later with the frac flowback water samples obtained from the Woodford shale.

The bench-scale experiments involved the evaluation of various additives, such as coagulants, flocculants, softening chemicals, sorbents, etc., various operating conditions, such as pH, concentrations, mixing times, settling times, temperatures, flow rates, etc. various separation equipment, such as filters, mixed-media deep filtration beds, cross-flow filtration, microfiltration, ultrafiltration, nanofiltration, reverse osmosis, etc.

Essentially, the key process steps for treating the frac flowback waters can be categorized as follows:-

- Clarification: Removal of suspended solids, oil & grease, microbiologicals, and dissolved organics (in some cases). Removal of Fe<sup>++</sup> may be included here since oxidation to Fe<sup>+++</sup> occurs readily in the presence of oxygen and Fe<sup>+++</sup> can cause precipitation and fouling in downstream applications either during re-use as Product-1 or in the desalination membrane modules used for producing Product-3 or Product-4.
- Softening; Removal of "hardness" ions, such as Ca, Mg, Ba and Sr, which may cause precipitation and plugging in downhole applications during re-use as Product-2 or in the desalination membrane modules used for producing Product-3 or Product-4.
- Desalination: Removal of dissolved salt ions, mainly NaCl using membranes used to produce product waters suitable for re-use as Product-3 or surface discharge as Product-4.

In the sections below, the approach for treating the flowback waters and the associated bench-scale experiments and results are described for the key process steps.

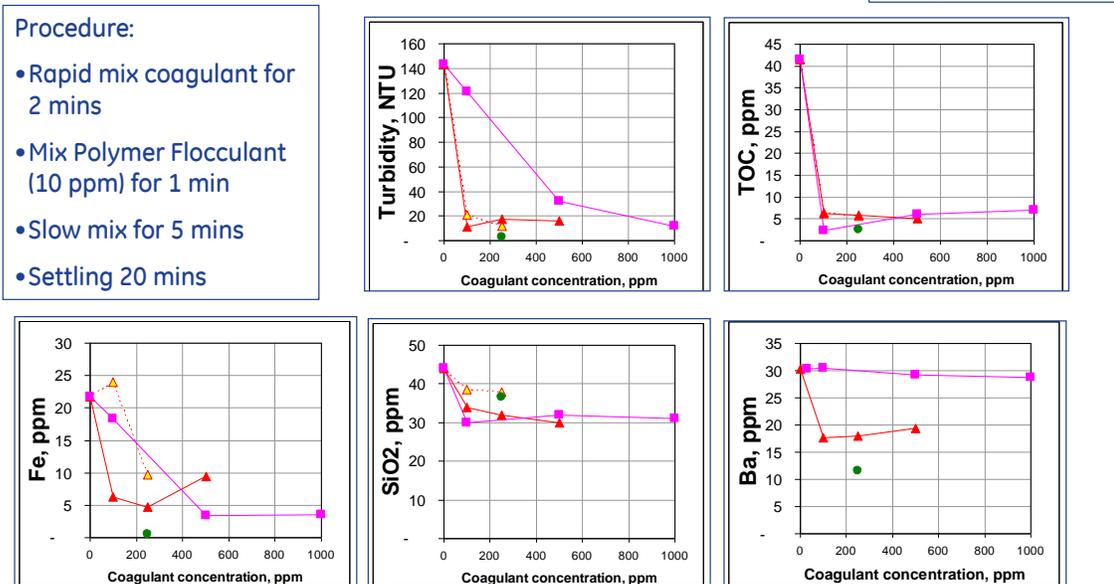
### 3.4.3 Process Step: "Clarify"

The purpose of this step is to remove contaminants in the flowback water to satisfy the downstream applications, either as Product-1 (cf. Figure 33) or as feed to membrane desalination processes. Note that the specifications for the membrane applications may be more stringent than for frac re-use with Product-1.

Various coagulants were evaluated at different operating conditions. Some of these bench-scale experiments with certain coagulants for the "composite" Days 1-14 water from Site-1 are shown for illustration in Figure 35. We observe that coagulation is effective at significantly reducing turbidity, TOC, Fe and Mn, as required for Product-1.

## Clarify: Evaluation of coagulants

Sample: Site-1 "composite" Days 1-14 water



Coagulants effectively remove target contaminants

Figure 35. Clarification of frac flowback waters. Results of bench-scale experiments with the "composite" Days 1-14 Woodford Site-1 sample.

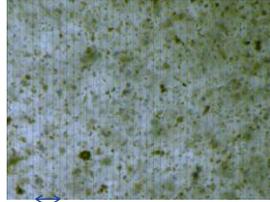
In Figure 36, the results of coagulation experiments with the Site-2 Day-26 sample are shown. For this experiment, the sample from the bottom of the 55-gal drum which had significant solids content was deliberately chosen to illustrate the effectiveness of the coagulation conditions. We observe that even this worst portion of the flowback water was effectively treated by these conditions.

## Clarify: Evaluation of coagulants

Water: Site-2 Day-26 Raw Bottom of jug



Day 26 Bottom of jug  
250ppm Coagulant-3 & 10ppm Flocculant  
Settled 30 minutes

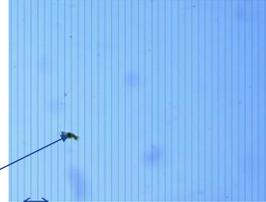


100 μm

NTU = 2098

TSS = 776

TOC = 18.4



floc

100 μm

NTU = 5.2

TSS = 136

TOC = 13

Figure 36. Clarification of frac flowback waters. Results of bench-scale experiments with the Day-26 Woodford Site-1 sample.

In Figure 37, the results of coagulation experiments with the Site-1 Day-1 sample are shown. As seen in Figures 16 and 17, the Day-1 sample had the highest total suspended solids (TSS) and very high total organic carbon (TOC) values relative to the “composite” Days 1-14 from Site-1 or the Day-26 sample from Site-2. We observe in Figure 37 that the coagulation conditions that were successful previously with the “composite” Site-1 Days 1-14 sample in Figure 35 and Day-26 Site-1 sample in Figure 36 were not as successful with this Site-1 Day-1 sample.

## Clarify: Evaluation of coagulants

Site-1 Day 1 Raw



NTU = 209

Site-1 Day-1 Settled 30 min  
500 ppm Coagulant-3  
5 ppm Flocculant



NTU = 89

Day 1 water difficult to treat!

Figure 37. Clarification of frac flowback waters. Results of bench-scale experiments with the Day-1 Woodford Site-1 sample.

However, when the supernatant liquid after flocculation and settling was passed through a novel GE-ultrafiltration membrane, the desired clarification was obtained, as shown in Figure 38. The technique was also effective for the Day-26 sample from Site-2, although such extra clarification may not be necessary in this case.

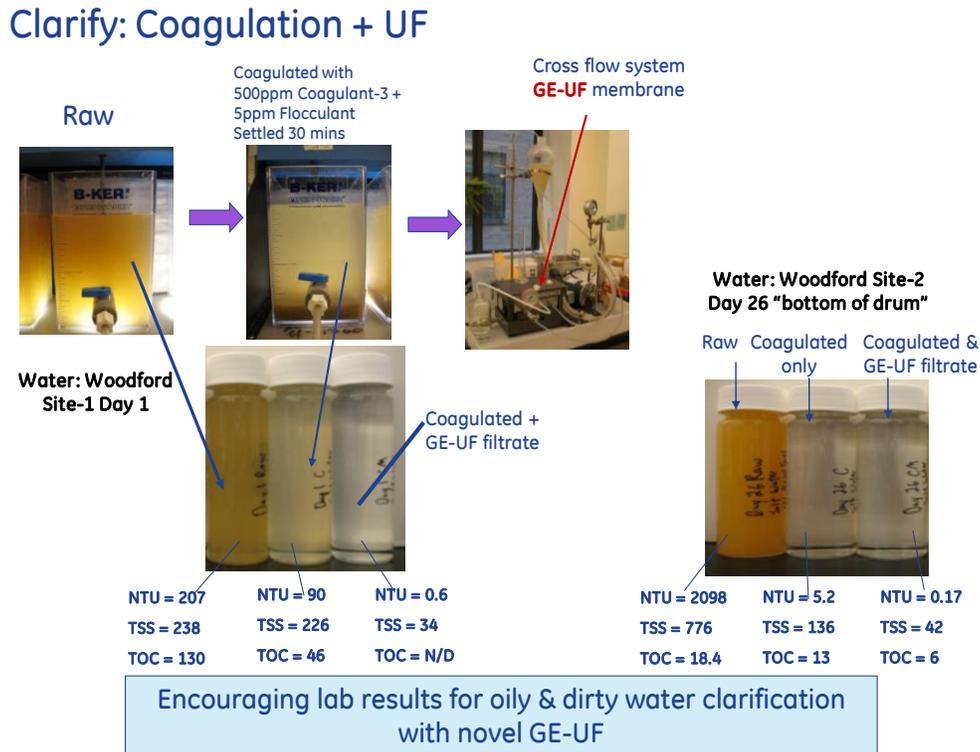


Figure 38. Clarification of frac flowback waters with coagulation and ultrafiltration. Results of bench-scale experiments with the Site-1 Day-1 and Site-2 Day-26 Woodford samples.

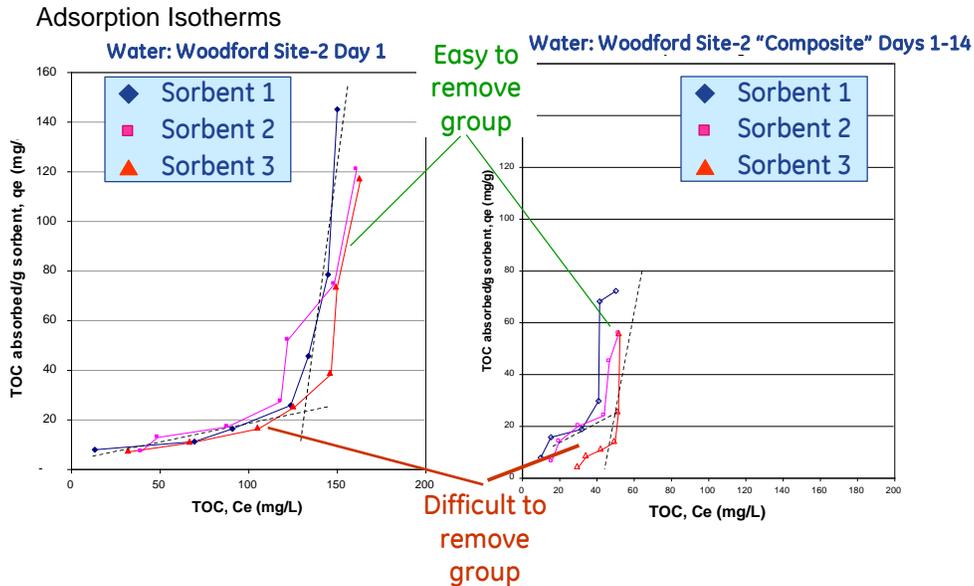
#### 3.4.3.1 Removal of Organics

The sources of organic compounds in the frac flowback water were described in Section 3.3.2 and were broadly classified as Free Oil & Grease, Dissolved Organics and Volatile Organics. In the data shown in Figures 35-38, we observed that it is relatively difficult to reduce the TOC for the Site-1 Day-1 water compared to the Site-2 Day-26 and Site-1 "composite" waters. It is very likely that the nature of the organics for the Site-1 Day-1 water is significantly different compared to the other later flowback samples, perhaps more contaminated by the Free Oil & Grease components.

For better understanding, various sorbents were evaluated. In Figure 39, the sorbent performance from isotherm experiments are plotted for similar experiments conducted with the Site-1 Day-1 sample and Site-1 "Composite" Days 1-14 sample. Interestingly, with the Day-1 sample, we observe two distinct regions in terms of efficacy of organics removal: (a) "easy" to remove organics from ~180 ppm to ~30 ppm TOC, and (b) "difficult" to remove organics down from ~30ppm TOC. This suggests to possibly different natures of the two sets of organ-

ics in the flowback sample. Moreover, we observe a similar behavior with the “Composite” Days 1-14 water sample, with an “easy” to remove group down to 20~30 ppm TOC and a more “difficult” to remove group down from ~20 ppm TOC. Very interestingly, the slopes for the “easy” regions of the adsorption isotherms for the two samples shown in Figure 39 are same, which indicates that the “composite” sample may be considered to be a diluted version of the Day-1 sample in this regard.

## Organics removal with sorbents: Lab-scale experiments



### Two “oil” groups – easy vs difficult to remove with sorbents!

Figure 39. Removal of organics from Woodford shale flowback samples. Comparison of adsorption isotherms of three sorbents for the Site-1 Day-1 sample and “Composite” Days 1-14 sample.

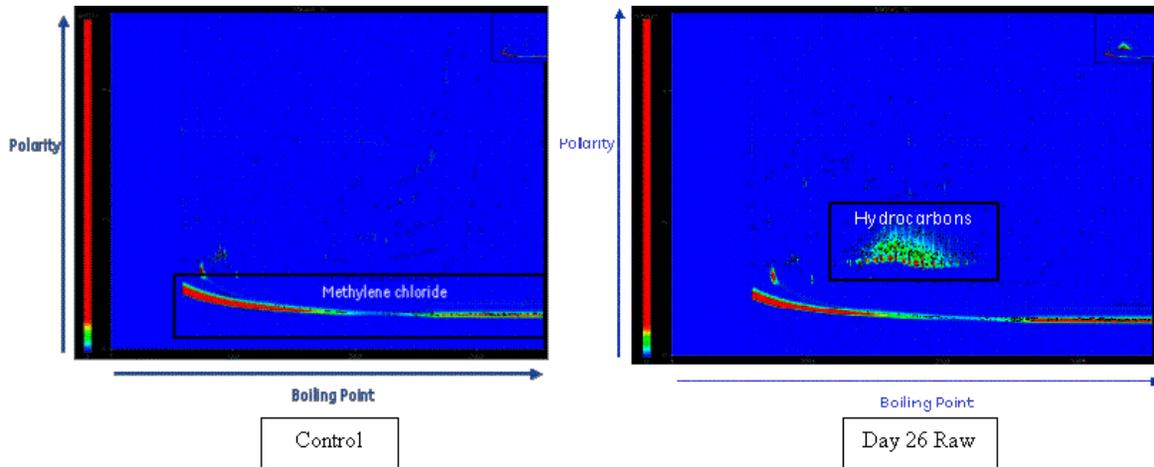
#### 3.4.3.2 Nature of the organics in frac flowback waters – novel analytical technique

The organic content of the flowback waters were initially measured by two techniques, namely via “hexane extraction” and by Total Organic Carbon (TOC), as reported in Figure 17. The “Hexane Extractables” method gives a measure of the components that are hexane soluble and is a good indicator of the free Oil & Grease content of the frac flowback water. The TOC measures the amount of combustible organic carbon present in the frac flowback water and is an indicator of dissolved and undissolved organics, including non-volatile and volatile compounds.

The “hexane extractables” and TOC methods are used routinely for estimating the organic content in waste waters. However, to understand the nature of these organic contaminants, we have used another technique developed by Hans Grade at GE Global Research that uses a 2-column gas chromatography (GC) method for separation of the components based on polarity and boiling point, followed by analysis with a Time of Flight Mass Spectrometer. In

this technique, 100 ml of the water of interest is mixed intimately with 20 ml of methylene chloride to allow extraction of the organic contaminants into the methylene chloride phase. After separation of the two layers, the organic contaminants are analyzed by the GCxGC MS method. A pure methylene chloride with 10 ppb methyl eiosoate was used as the Control sample for comparison.

In Figure 40, the GCxGC MS plots for the Day-26 raw frac sample and the Control sample are shown in the 2-dimensional format of Polarity x Boiling Point. We notice the location of different hydrocarbons on the plot for Site-2 Day-26 water.



**Figure 40. GCxGC-MS 2-D plots for the Control and Day-26 (frac) raw water. Note the presence of hydrocarbons of various polarities and boiling points (molecular weight) in the Site-2 Day-26 sample.**

The GCxGC-MS data may also be plotted in a 3-D format to indicate the magnitude of the response, as shown in Figure 41 for the Control sample. It should be noted that although the magnitude could be an indicator of the concentration of the organic contaminant (or fragment), it may be influenced by a variety of others factors. Hence, these 3-D plots are best used as qualitative indicators.

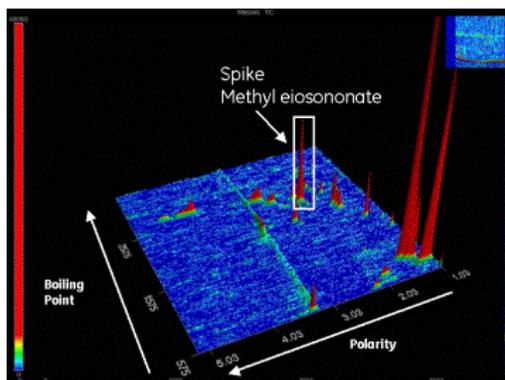


Figure 41. GCxGC-MS 3-D plot for the Control methylene chloride (with 10 ppb methyl eisononate).

Similarly, GCxGC-MS 3-D plots for the Site-2 Day-26 and Site-1 Day-1 frac water field samples are shown in Figure 42. The corresponding data for the hexane-extractables and TOC methods shown in Figure 17 are also reproduced in Figure 42. We observe that the Site-1 Day-1 sample has more polar hydrocarbon compounds and also higher intensities. This corresponds to higher total organic carbon in the Site-1 Day-1 raw water compared to Site-2 Day-26 sample.

## Hydrocarbon removal analysis

Novel sample analysis based on GC x GC + ToFMS technique  
(Instrument: LECO Pegasus 4D )

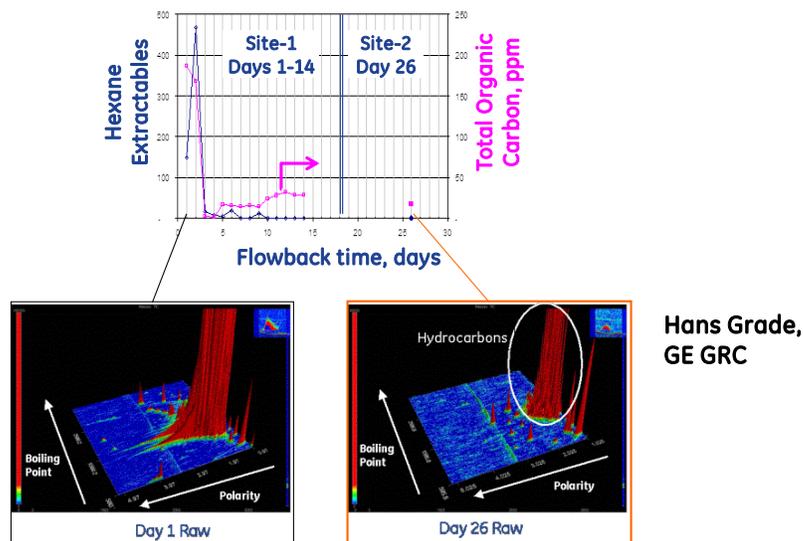
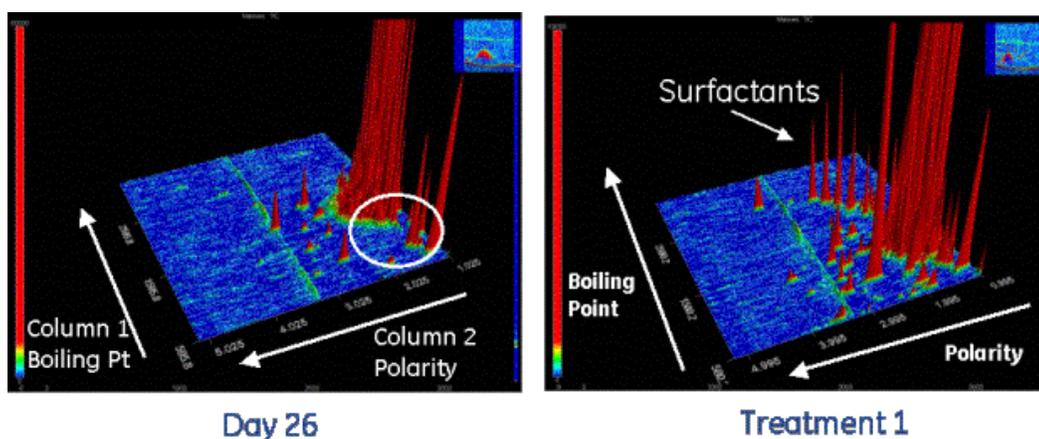


Figure 42. GCxGC-MS 3-D plot for the Day-26 and Day-1 frac water field samples. Day-1 sample has more polar hydrocarbons and in general, higher intensities corresponding to the overall higher TOC content.

## Evaluation of various treatment methods for removing organics in frac flowback waters

A series of 1-liter jar experiments were conducted with the frac flowback field samples using a variety of coagulants, flocculants, adsorbents, and oxidants and for various operating conditions (time, mixing conditions). Samples were collected during these experiments and analyzed by the above mentioned GCxGC-MS method to evaluate the effect of the treatment method on appearance or disappearance of organic species. For example, in Figure 43, the GCxGC-MS plot for the water sample after Treatment 1 is compared to the original raw Site-2 Day-26 water sample. We observe that the Treatment 1 introduced certain species that were shown to correspond to surfactant molecules.



**Figure 43. Effect of Treatment#1 on the organic contaminant levels of the Day-26 frac flowback water sample. Observe the appearance of peaks associated with surfactant molecules.**

Similarly, Treatment method 5 and Treatment method 13 are compared in 2-D GCxGC-MS plots in Figure 44. We observe that Treatment 5 has effectively removed a portion of the hydrocarbons found in the original Day-26 raw water, while Treatment 13 has significantly diminished the intensities of the hydrocarbon peaks relative to raw and after Treatment 5.

The effect of operating time for Treatment #13 on the level of organic contaminants in the frac flowback water is illustrated in Figure 45. We observe that the intensities of the peaks corresponding to organic contaminants diminishes significantly for longer operating times.

From the above results it is clear that the novel GCxGC +ToFMS analytical technique provides a powerful means to evaluate the effect of various treatment methods on the presence and disappearance of various organic species. However, it should be noted that the nature of this research is still in its infancy. More work is required to quantitatively link the effectiveness of any treatment method on the removal of particular organic species that are undesirable for product quality specifications for frac re-use or impact on desalination membrane fouling.

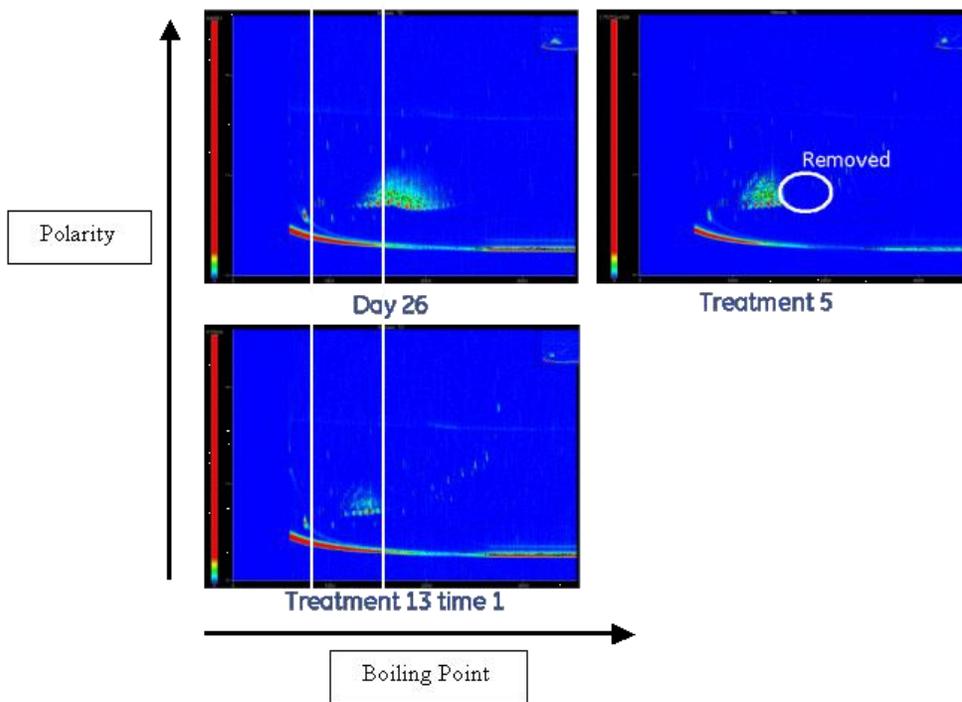


Figure 44. Comparison of GCxGC-MS 2-D plots for Day-26 raw water and after Treatment#5 and Treatment#13.

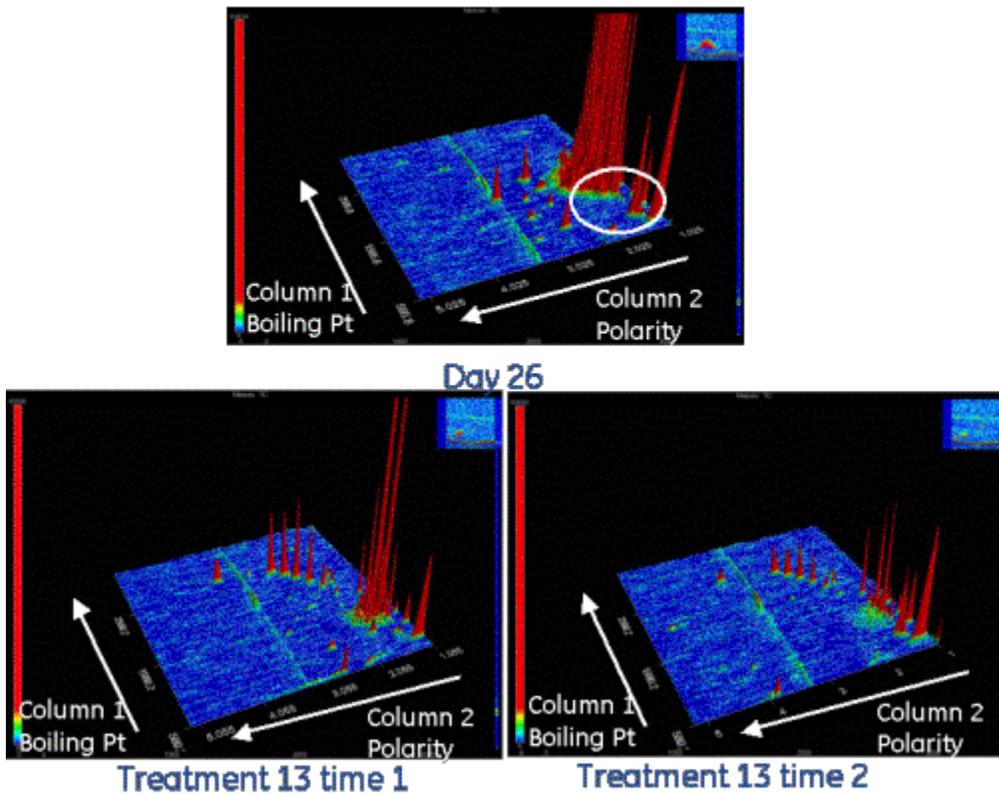


Figure 45. Comparison of GCxGC-MS 3-D plots for Day-26 raw water and after Treatment#13 for two different times.

#### 3.4.4 Process Step: "Soften"

The removal of "hardness" ions, such as Ca, Mg, Ba and Sr, may be accomplished by precipitation methods, such as lime softening or membrane methods, such as nanofiltration that selectively reject the divalent and trivalent ions. The lime-softening process, if properly designed would provide water recoveries in the range of >95%, which satisfies the requirements in Figure 30. We evaluated nanofiltration via modeling with the GE Winflows membrane system design and simulation software<sup>20</sup> using technical performance data for GE's nanofiltration membranes. For the frac feed water sample analyses reported in Table 3, although the removal of hardness was >80%, the water recoveries were in the range of 50~80%, which is much lower than the product specifications in Figure 30. Hence, we have focused our efforts on evaluating only lime-softening for softening frac flowback waters.

Lime softening has been industrially used for more than a hundred years. It may be operated in the "cold" mode or "hot" mode. Although the "hot" mode requires less chemicals, choosing the "cold" mode will provide robustness to our conceptual process in handling frac flowback waters from a variety of frac sites.

The principles and process of lime softening are best explained on the GE Water website<sup>21</sup>. Hence, only a summary is provided below.

When hydrated lime,  $\text{Ca(OH)}_2$ , is added to the water being treated, the  $\text{Mg}^{++}$  ions are precipitated as  $\text{Mg(OH)}_2$ . Noncarbonate or permanent calcium hardness, if present, is not affected by treatment with lime alone. The frac flowback water sample analyses shown in Table 3 indicate a high level of noncarbonate hardness – the total hardness/"M" alkalinity ratio is ~4-5 for the three samples under consideration. In such cases, soda ash ( $\text{NaCO}_3$ ) is added to precipitate the  $\text{Ca}^{++}$  as  $\text{CaCO}_3$ .

Bench-scale experiments were conducted by addition of  $\text{Ca(OH)}_2$  and  $\text{Na}_2\text{CO}_3$  to 1-liter jars containing the frac flowback sample. The results for the Site-1 Day-1 and Site-1 "Composite" Days 1-14 samples are shown in Figure 46. Similar data was obtained for the Site-2 Day-26 sample (reported later in Table 5). We observe that lime softening conditions are able to significantly reduce the hardness levels to meet the specifications for Product-2 and the pretreatment levels required for desalination membrane processes.

The process equipment required for precipitation softening are vessels with mixing equipment to contact the feed water with the lime initially and then with soda ash. After sufficient contacting, the precipitate is allowed to settle and the clear liquid is filtered. The settled solids or sludge needs to be compacted to reduce the water content and lower the waste handling and disposal costs. A combination of sludge compaction and filtration is used typically to obtain wastes containing ~30% solids. Further reduction of the water content may require some means of evaporation. The relative costs of locating such sludge drying processes on-site versus the waste disposal costs need to be weighed on an individual frac flowback site basis.

# Clarify + Soften: Lab-scale experiments

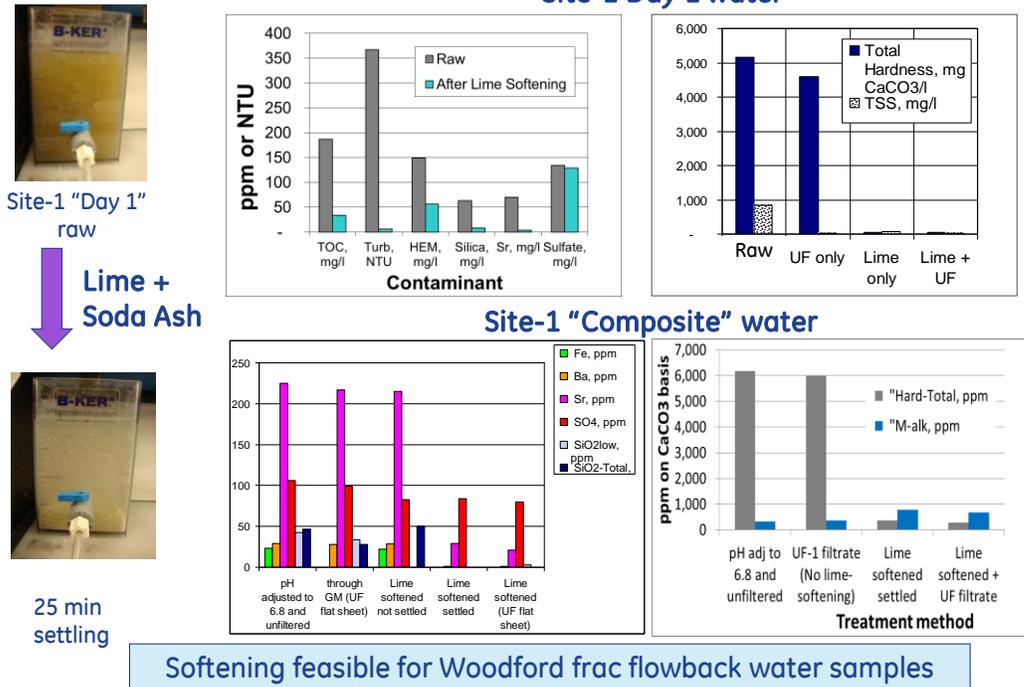


Figure 46. Clarification of frac flowback waters with coagulation and ultrafiltration. Results of bench-scale experiments with the Site-1 Day-1 and Site-2 Day-26 Woodford samples.

The expected water recovery after such a lime-softening process is expected to be >95%.

Mass balances were conducted for a 50-gpm frac flowback water treatment system to determine the amounts of lime & soda ash required and the amount of waste stream generated.

For the Site-2 Day-26 stream shown in Table 3, the amounts of Ca(OH)<sub>2</sub> and Soda Ash required per bbl of feed water would be 0.38 lbs and 0.56 lbs, respectively on a dry basis. The amount of sludge (30% solids) produced would be 3.68 lbs/bbl feed processed, i.e. 3.2 short tons/day. Assuming disposal costs of \$70/ton at a non-hazardous disposal site located within 50 miles and transportation costs of \$5/mile, the waste disposal costs are estimated to be in the range of \$0.15/bbl of feed.

For the Site-1 Composite Days1-14 sample, which contains a higher level of hardness, the amounts of Ca(OH)<sub>2</sub> and Soda Ash required per bbl of feed water would be 0.50 lbs and 1.91 lbs, respectively on a dry basis. The amount of waste generated would be 7.84 lbs/bbl water processed, i.e. 6.7 short tons/day. The waste transportation and disposal is estimated in the range of \$0.30/bbl of feed.

### 3.4.5 Desalination Membrane performance

For Product-3 and Product-4, that require desalination to TDS levels <20,000 ppm and <500 ppm, respectively, the performance of membrane desalination was evaluated via modeling using the GE Winflows membrane system design and simulation package<sup>20</sup>. Various membrane materials and system design configurations were considered to increase water product recovery. The methodology is illustrated in Figure 47 for a feed solution with composition similar to that obtained after pretreating (lime softened and filtered) Site-2 Day-26 sample. This feed rate was 50 gpm and contained 35K ppm TDS, while the desired product has TDS <500 ppm, i.e. meeting Product-4 quality requirements (cf. Figure 30). We observe that by appropriate choice of membrane system designs, it is possible to increase the recovery from 49% using the standard seawater-desalination design to as high as 61.5%. The retentate concentration correspondingly increased from 68K ppm to 90K ppm TDS for these conditions. This has implications on overall system recovery and costs of the overall flowback water recovery process, as will be discussed under Task 6. The increase in the number of stages and process complexity increases capital equipment costs in terms of pumps, membrane modules, interconnected piping and control equipment. Hence, trade-offs of higher recovery vs. higher equipment costs needs to be considered.

## Desalination: Increasing water recovery by Multi-staging

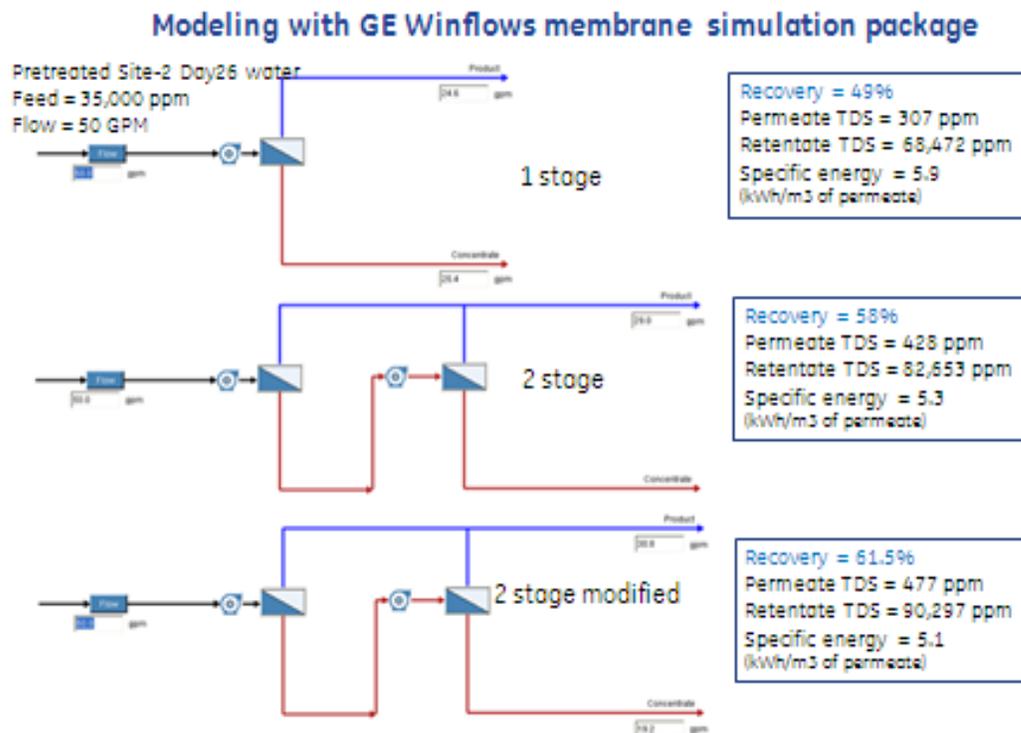
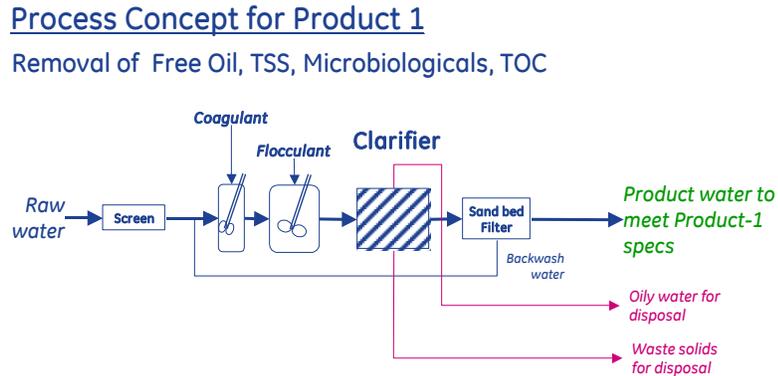


Figure 47. Maximizing RO-desalination water recovery of pretreated Site-2 Day-26 flowback water via simulation studies using GE Winflows software<sup>20</sup>.

### 3.4.6 Process Flowsheets

Using the information from the bench-scale experiments for the various pretreatment steps, detailed conceptual flowsheets for the treatment processes were constructed for each of the Products 1-4 under consideration. For the case of producing Product-1 quality water, the conceptual flowsheet is illustrated in Figure 48.



**Figure 48.** A conceptual process flowsheet for treating frac flowback waters to produce waters meeting Product-1 quality specs (cf. Figure 30).

Similarly, process flowsheets were constructed to meet the respective quality requirements for Product-2, Product-3 and Product-4. These were evaluated for technical performance, costs and mobility for a 50-gpm feed (frac flowback) mobile rig system. Technical performance evaluation included mass and energy balances, including waste generation and handling. Costs included capital expenses for equipment and assembly, and operating expenses for amortization of capital equipment, rig-setup labor, chemicals, membranes, power, and waste removal. Mobility included the preliminary assessment of the rig configurations suitable to treat 50 gpm of the frac flowback water.

The treatment costs to produce Product-4 - the most challenging and most expensive - is illustrated in Figure 49. As described earlier, treatment costs include  $C_{Setup}$  (Cost of mobile rig transportation and setup at the frac site) and  $C_{Process}$  (Cost associated with the capital and operating expenses related to the process steps). It does not include the cost of product- and concentrate-disposal. The labor costs associated with setting up the mobile rig are included in  $C_{Setup}$  and thus in the  $C_{Treatment}$  value. However, the rig operating labor for treating flowback water has not been included since these costs may be accounted differently by different producers as the rig may be run by operators handling multiple responsibilities at the frac site.

We observe the following in Figure 49:

- The treatment cost,  $C_{\text{Treatment}} < \$2/\text{bbl feed}$ , which was the target for our verification of success criteria (cf. Figure 32)
- Nearly 75% of the operating costs are related to “fixed” charges (capital equipment related and rig transportation & setup), 18% due to chemicals and solid wastes disposal, while cost of replacement membranes and electricity costs were only 2% and 5%, respectively. This indicates that for such low throughput mobile rigs, optimizing membrane performance to reduce power consumption will not have significant impact on the overall economics. What really matters is that the overall water recovery is improved while keeping the system capital costs low.

## Operating cost breakdown for 50 gpm mobile membrane rig

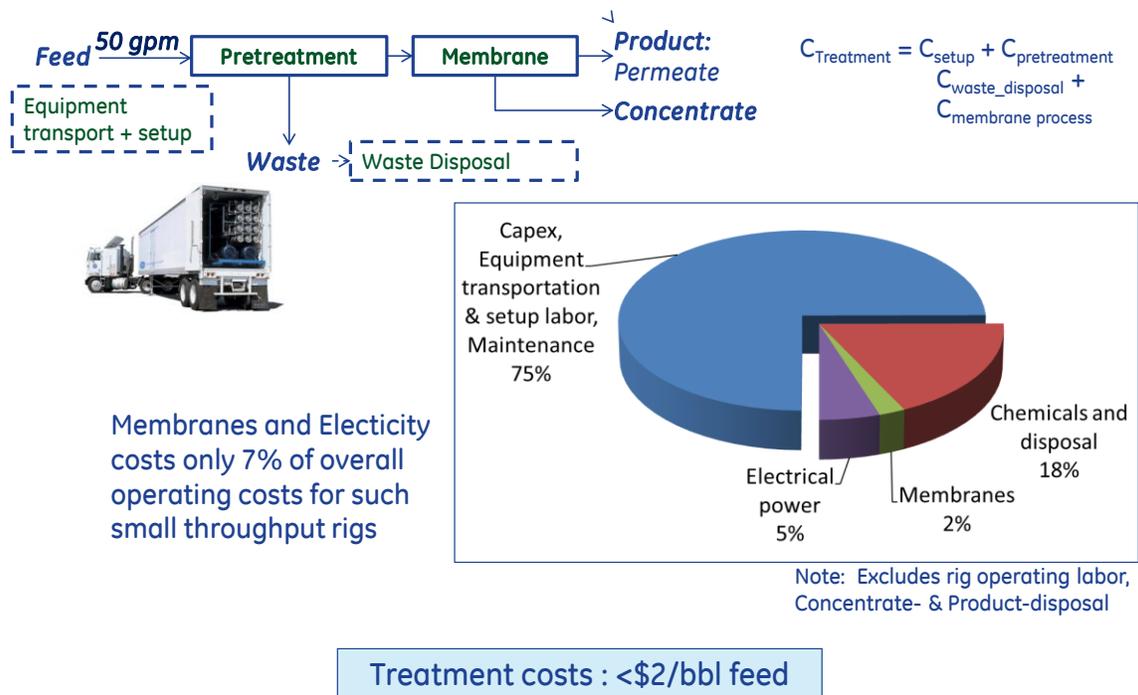


Figure 49. Operating cost breakdown for a 50 gpm mobile membrane rig capable of producing <500 ppm TDS product

### 3.4.7 Conclusions from Task 4:

The results of the bench-scale experiments, membrane system simulation and system cost analysis indicated the following in relation to the verification of success criteria for this project (cf. Figure 32):

- Technical Performance: There is a high level of confidence that the conceptual processes will be effective to yield the Products-1, -2, -3 and -4 of desired quality since these process flow schemes were constructed based on the bench-scale experimental studies on

the individual separation technologies using actual frac flowback samples. Many of the initial concerns were mitigated by appropriate choice and verification of process operating conditions in the lab-scale experiments.

- **Cost Performance:** The estimated costs for the four product options were within the cost criterion of < \$2/bbl that was established in Task 2, and in line with preliminary feedback on customer expectations. The cost estimations were based on reliable values obtained either from vendors or internal cost information for the desired equipment. Other cost factors, such as costs of electricity, type and cost of labor, waste handling & disposal, were also obtained either from appropriate vendors or internal cost information.
- **Mobility Performance:** Based on vendor information on sizes and operations of the various equipment identified for the conceptual processes, and internal data on mobile rig operations, 50-gpm mobile rig configurations may be achievable for the four products under consideration.

Based on these technical-, economic- and mobility-feasibility analyses on currently available customer information for product quality and cost information, and the supporting lab-scale experimental results, the recommended course of action for the critical go/no-go decision was to **go ahead** with the project towards Tasks 5 and 6.

### **3.5 Task 5: Obtain bench-scale experimental data suitable for process modeling**

#### **3.5.1 Objectives and Approach**

The objectives were:-

- Obtain membrane performance parameters necessary for system performance modeling.
- Demonstrate the efficacy of the downselected pretreatment methods to treat the field samples for low fouling of the RO-membranes during desalination.

Desalination experiments were conducted in the membrane-module testing rig shown in Figure 50. The rig consists of a feed tank, a high pressure pump, a membrane module housing, and relevant pressure, flow, conductivity and temperature sensors. Water is pumped from the feed tank through the membrane module inside the housing. A portion of that feed water permeates through the membrane (called “permeate”). The remaining portion (called “retentate”) is returned to the feed tank. A cooling bath and appropriate heat exchange equipment ensure that uniform temperature is maintained during the entire course of the experiment (note that the pumping energy results in a significant temperature rise of the re-circulating water).

The independent parameters are:

- Feed composition
- Feed rate

- Pressure
- Temperature
- Membrane module parameters: Membrane type, Surface area, Internal geometry

The dependent & measured parameters are:-

- Permeation rate
- Permeate concentration
- % recovery per pass

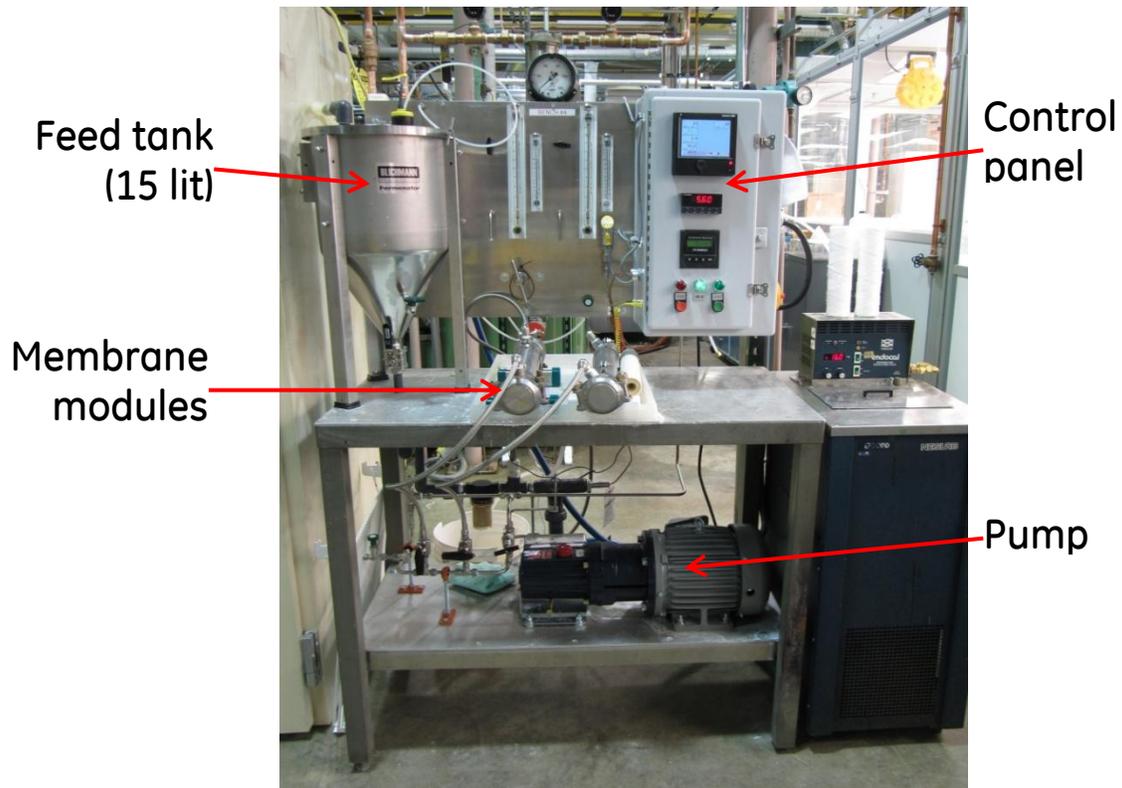


Figure 50. Membrane module testing rig for conducting desalination experiments with pretreated field frac flowback samples at GE Global Research.

Modes of operation:

- Closed circuit: The permeate is returned to the feed tank. In this case, the net concentration in the feed tank essentially remains constant since the retentate and permeate streams are re-mixed. This mode is useful for determining the stability of the membrane performance as a function of time. We used this mode to evaluate the possible fouling of the RO membranes over a period of 24 hours, as described below.
- Open circuit: The permeate is not returned to the feed tank. In this case, the loss of desalinated permeate volume results in a net increase in TDS concentration in the

feed tank. This mode is useful for determining the membrane performance properties as a function of feed concentration.

The membrane performance parameters of interest are:

- Water-flux parameter: This is frequently referred to as “A-value” in reverse osmosis literature. A high value of this parameter is preferred as it implies a low membrane surface area requirement for the given separation duty, and thus lower costs and smaller footprint for the ultimate application. Conversely, for a given membrane module configuration (fixed area), a high A-value implies lower pumping pressure requirements.
- Salt-flux parameter: This is frequently referred to as “B-value” in reverse osmosis literature. A low value is preferred for this parameter as it implies low permeation of the salt species through the membrane, which results in a more purified permeate product.
- Salt-rejection parameter: This parameter is an indicator of the separation efficiency of the RO membrane at the operating conditions. A high value is preferred as it yields a more purified permeate product.

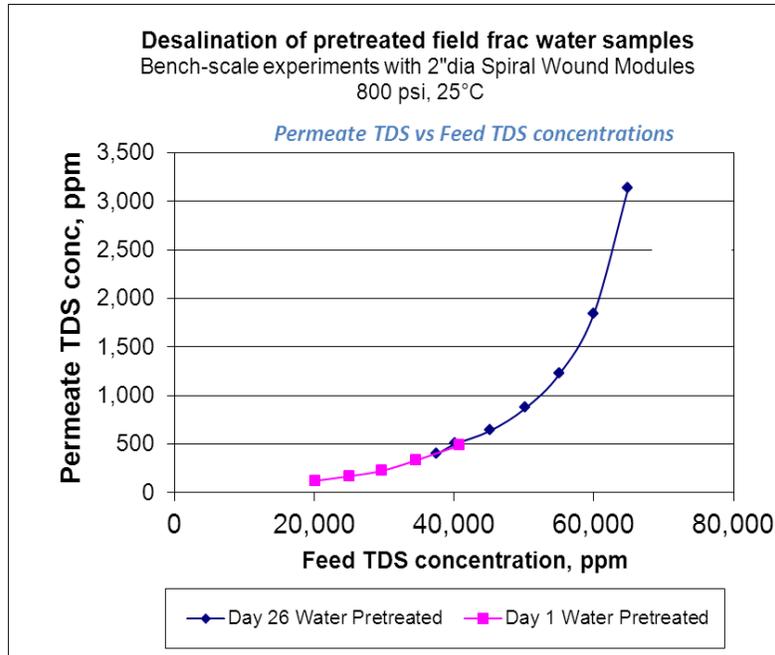
These parameters are used for modeling large-scale membrane module performance and also for membrane-system level performance modeling.

### **3.5.2 Membrane performance parameters vs. Feed composition**

The field sample Site-2 Day-26 was subjected to appropriate pretreatment process steps to produce 14 liters of solution (approx. 95% recovery) with a TDS of ~33,000 ppm. Similarly, the field sample “Day-1” was subjected to appropriate process steps to produce 7 liters of solution (approx. 95% recovery) with a TDS of ~20,000 ppm. Desalination of this treated water was performed using spiral wound modules (2” diameter, 4.5 ft<sup>2</sup> membrane area) with high-selectivity membranes that are typically used for seawater desalination to produce very low TDS permeate product (<500 ppm TDS).

The experiments were conducted in the open circuit mode to obtain the profiles of the desired membrane performance parameters as a function of feed composition. The permeate TDS for both of the field sample runs are plotted in Figure 51. For the Site-2 Day-26 sample, we observe that the feed concentration increased from 37,500 ppm TDS to 64,000 ppm TDS, with a net permeate recovery of 42% at an operating pressure of 800 psi. Further experimentation was stopped since the permeation flow rate was too low due to the high osmotic pressure of the feed solution as its concentration increased. For the Site-1 Day-1 sample, we observe that the feed concentration increased from 20,000 ppm TDS to 42,000 ppm TDS, with a net water permeate recovery of about 51%. Further recovery would have been possible but the experiment had to be stopped because of the low levels in the feed tank. Nevertheless, it is interesting to note the smooth nature and overlap of the permeate TDS vs. feed TDS profile for the two different pretreated field flowback samples in Figure 51, which is due to

the membrane properties and the cleanliness of the pretreated field frac flowback samples. We observe that the permeate TDS concentration rises rapidly as the feed TDS concentration rises for this membrane.



**Figure 51. Permeate TDS vs. Feed TDS for the 2" spiral wound RO module runs using 10~15 liters of pretreated field frac flowback samples. See text for details.**

The membrane performance parameters, namely water-flux, salt-flux and salt-rejection vs. Feed TDS concentration for these two pretreated field frac flowback samples are shown in Figures 52, 53, and 54, respectively.

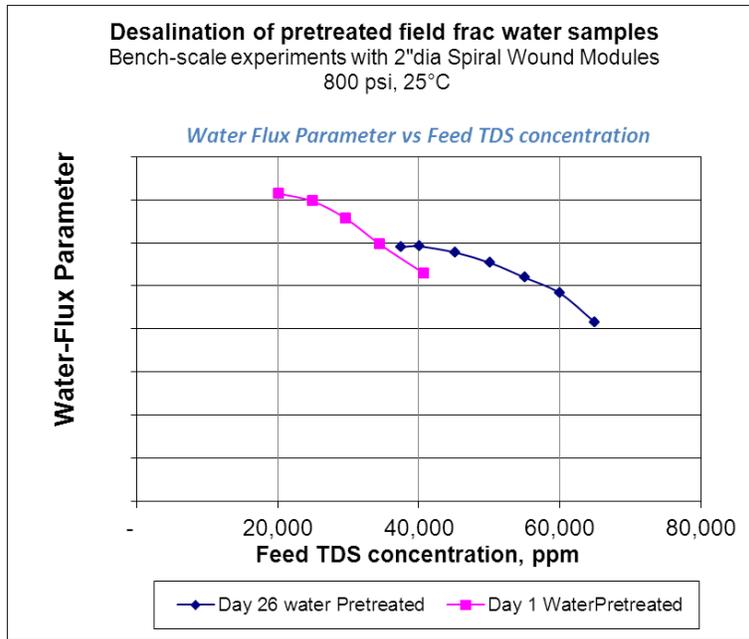


Figure 52. Water flux parameter vs. Feed TDS for the 2" spiral wound RO module runs using 10~15 liters of pretreated field frac flowback samples. See text for details.

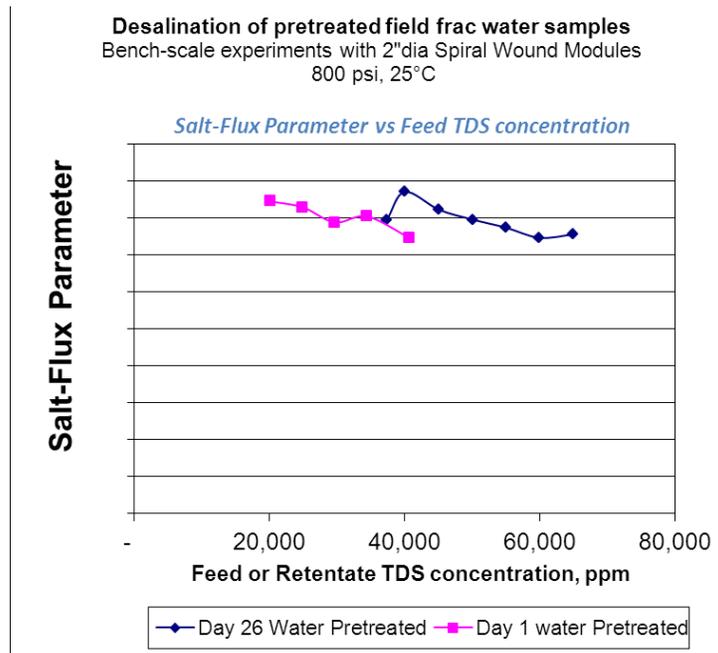


Figure 53. Salt-flux parameter vs. Feed TDS for the 2" spiral wound RO module runs using 10~15 liters of pretreated field frac flowback samples. See text for details.

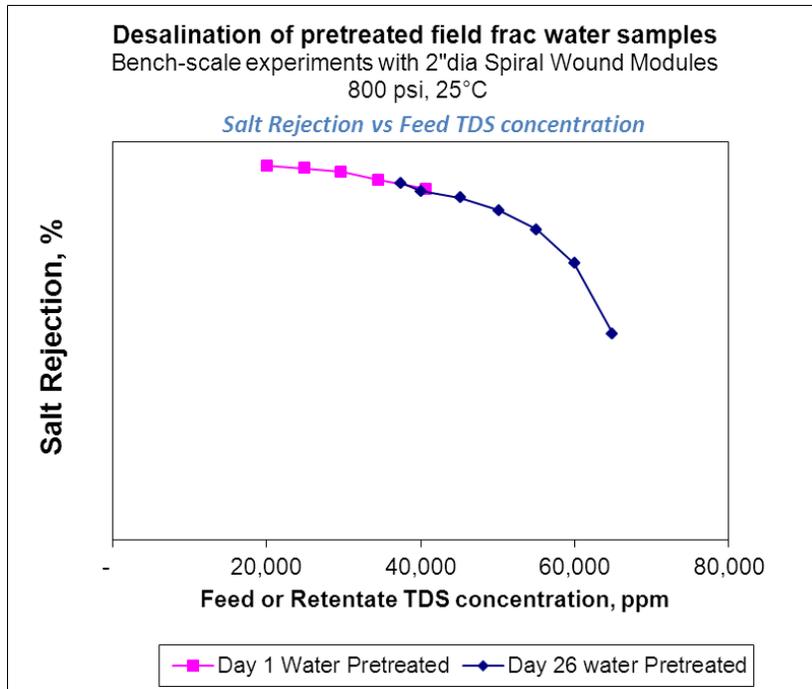


Figure 54. Salt-rejection parameter vs. Feed TDS for the 2" spiral wound RO module runs using 10~15 liters of pretreated field frac flowback samples. See text for details.

As mentioned earlier, these parameters are useful for modeling large-scale membrane module performance and also for membrane-system level performance modeling. Similar data were gathered for other membrane types; especially those with higher flux (perhaps lower salt rejection) to yield lower quality (higher TDS) permeate suitable to meet the Product-3 quality requirements (cf. Figure 30).

### 3.5.3 Evaluation of Desalination Membrane Fouling

The pretreated Site-2 Day-26 field frac flowback sample was used to evaluate the effectiveness of pretreatment on the fouling of a desalination membrane over a period of 24 hours. The parameters considered were the water-flux, salt-flux and salt-rejection. The results for the pretreated Site-2 Day-26 field sample were compared to those for pure 35,000 ppm TDS solution prepared with de-ionized water and pure NaCl. The membrane considered was the high-selectivity desalination membrane typically used for seawater desalination to produce very low TDS permeate product (<500 ppm TDS) in the spiral wound modules (2" diameter, 4.5 ft<sup>2</sup> membrane area) format.

#### Experimental procedure:

For the Site-2 Day-26 field frac flowback sample, the fouling runs shown below in Figures 55-57 were obtained over 24 hours by operating the system of Figure 50 in a closed circuit mode (Note that immediately following this operation, the system was operated in the open circuit mode to obtain the performance vs. feed TDS profiles reported previously in Figures 52-54).

After the Site-2 Day-26 sample run, the entire rig assembly shown in Figure 50 was purged and flushed with de-ionized water several times. A new membrane module containing the same membrane type and configuration, and manufactured at the same commercial facility was installed in the membrane housing. This module was flushed with de-ionized water and other treatments were performed as per membrane manufacturer's recommendations. Then about 15 liters of the NaCl solution in de-ionized water was introduced and the solution was circulated through the system at low pressure to mix the feed solution in the system. The feed concentration was approximately 35,000 ppm TDS when high pressure of ~800 psi was applied and the permeation process was allowed to continue in the closed circuit mode.

The profiles of the 3 parameters of interest, namely water-flux, salt-flux and salt-rejection are shown normalized to the initial values for the pretreated "Day-26" field frac flowback sample with 37,500 ppm TDS and the comparative 35,000 ppm TDS pure NaCl in de-ionized water in Figures 55, 56, and 57, respectively.

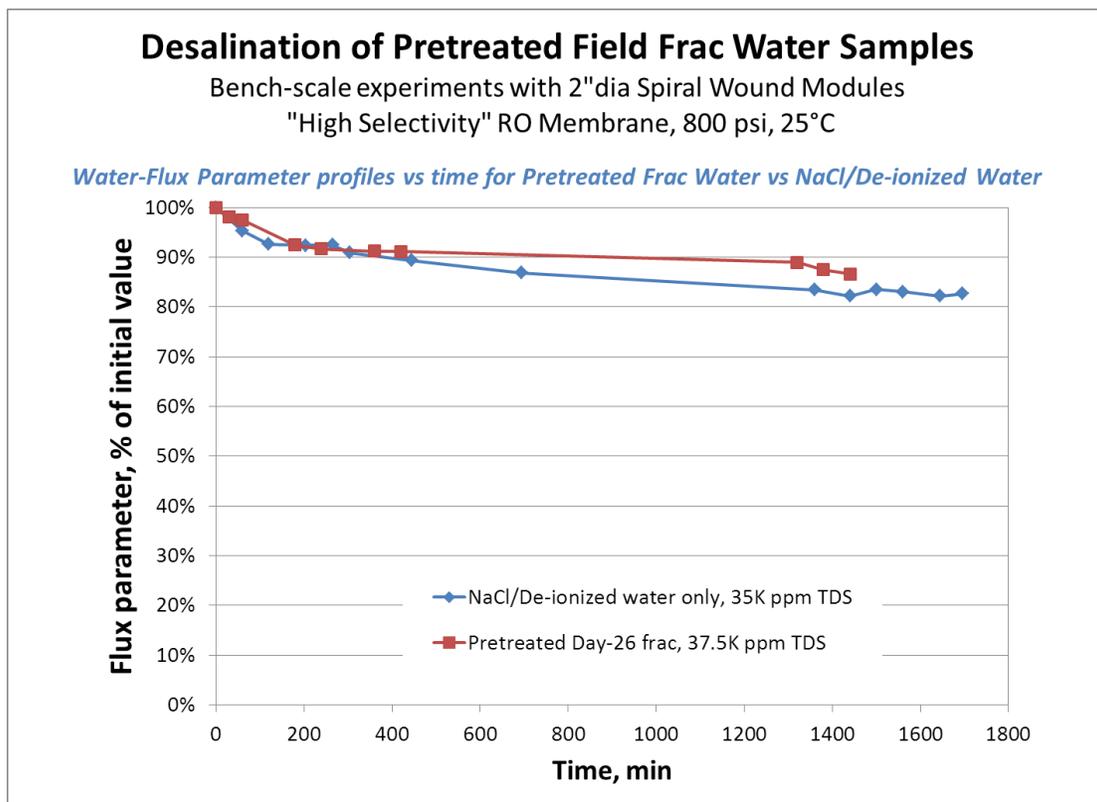


Figure 55. Comparison of water-flux parameter change due to desalination membrane fouling for pretreated Site-1 Day-26 field frac flowback sample and pure NaCl/de-ionized water solution.

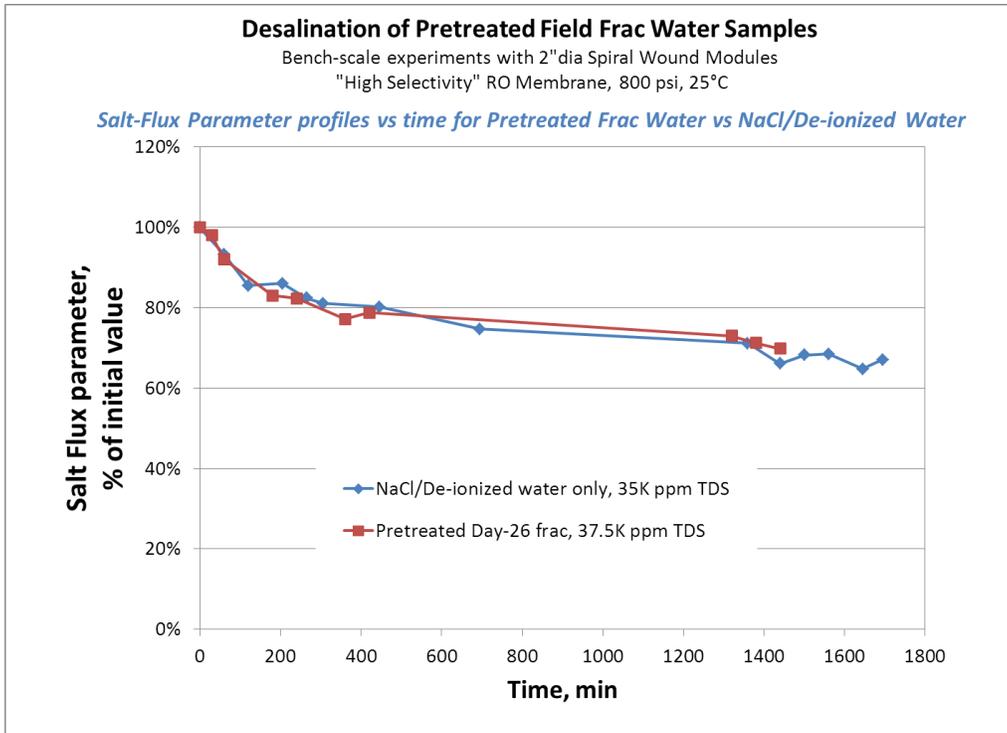


Figure 56. Comparison of salt-flux parameter change due to desalination membrane fouling for pretreated "Day-26" field frac flowback sample and pure NaCl/de-ionized water solution.

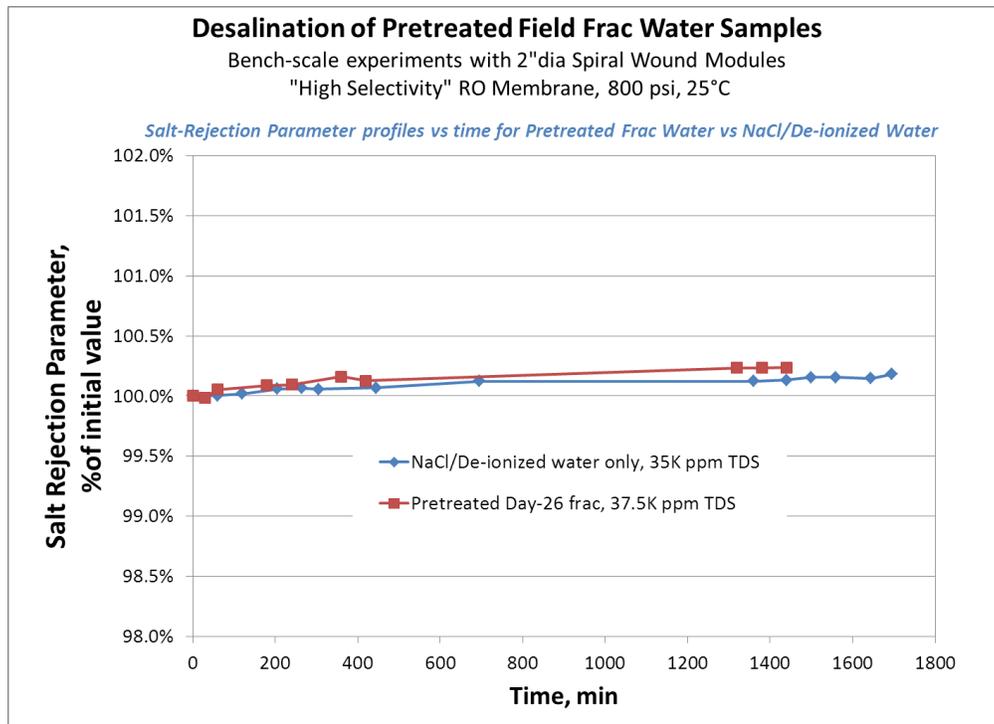


Figure 57. Comparison of salt-rejection parameter change due to desalination membrane fouling for pretreated "Day-26" field frac flowback sample and pure NaCl/de-ionized water solution.

The composition analyses for the Site-2 Day-26 before and after these 24-hour membrane fouling experiments are shown in Table 5. We observe the extent of hardness (Ca, Mg, Ba, Fe, Sr) removal by the pretreatment methods, and the permeate product quality (<500 ppm TDS).

**Table 5. Composition analyses for the Site-2 Day-26 waters: raw, pretreated by softening, and after 24-hr membrane fouling test.**

Description	Raw	lime softened, pH adjusted & filtered through 1um	Final Retentate after RO	Permeate
"B, ppm	24.8	23	22.6	8.35
"Ba, ppm	30.7	0.147	0.161	<0.1
"Ca Hard, ppm	1160	37.4	34.7	<5.0
"Cl, ppm	21600	21200	19700	243
"Cond, ppm	54000	53500	50200	869
"Fe, ppm	184	<0.5	<0.5	<0.5
"HEM, ppm	2100	<6.0	<6.0	<6.0
"Hard-Total, ppm	301	563	545	<10.
"K, ppm	559	316	303	<5.0
"M-alk, ppm	749	334	340	22.7
"Mg Hard, ppm	1.19	518	503	8.21
"Mn, ppm	<0.6	<0.1	<0.1	<0.1
"Na, ppm	16900	17200	16400	221
"Ni, ppm	0.112	<0.1	0.309	<0.1
"SO4, ppm	29	31	29	<1.0
"SiO2 reactive, ppm	48	40	36.2	<2.0
"SiO2-Total, ppm	185	39.9	39.9	<5.0
"Sr, ppm	152	6.43	6.15	<0.1
"TDS, ppm	32700	30700	29100	440
"TOC, ppm	18.4	6	6.1	<1.0
"TP, ppm	62.4	41.1	22.3	<4.0
"TSS, ppm	776	18	71	<10.
Turb, NTU	2150	0.63	0.75	0.24
"pH, ppm	7.36	7.54	7.84	8.34
"NH3-Free, ppm		53	49.3	1.89

Observations and Conclusions:

There is usually a decline of ~10% in water-flux parameter during the initial 6~ 8 hours (perhaps due to pressure compaction) as seen with the profiles of both the Site-2 Day-26 and control DI water with only NaCl (cf. Figure 55). But the trend after this initial period is important to observe from a fouling perspective. A steady decrease in performance over time would have indicated fouling of the membrane surface. However, we observe similar changes in performance over the initial 24-hour period for the two water solutions in Figures 55, 56 and 57. This indicates that there is insignificant fouling of the desalination membrane by the contaminants in the pretreated field frac flowback sample compared to the control sample. In other words, the downselected pretreatment conditions were effective in removing potential fouling contaminants from the field frac flowback sample (at least for this field sample and under these desalination experimental conditions).

### 3.6 Task 6—Develop system performance and cost models

#### 3.6.1 Objectives and Approach:

The key objectives were:-

- Cost modeling for a mobile unit for low-TDS flow back water recovery
- Determination of economical “cut-off” point for low-TDS water recovery process for flowback water treatment

System cost models were developed for the mobile rig configurations for the four products under consideration (cf. Figure 30). However, in the following discussions, only the costs for membrane desalination systems used for Product-3 and Product-4 will be reported as they encompass the pretreatment steps used for Product-1 and Product-2 as well as the membrane desalination steps.

In Figure 58, the system configurations for the Conventional frac flowback disposal via underground Class II injection and the Flowback Water Recovery Process (FWRP) considered in this project are described.

### System cost estimations

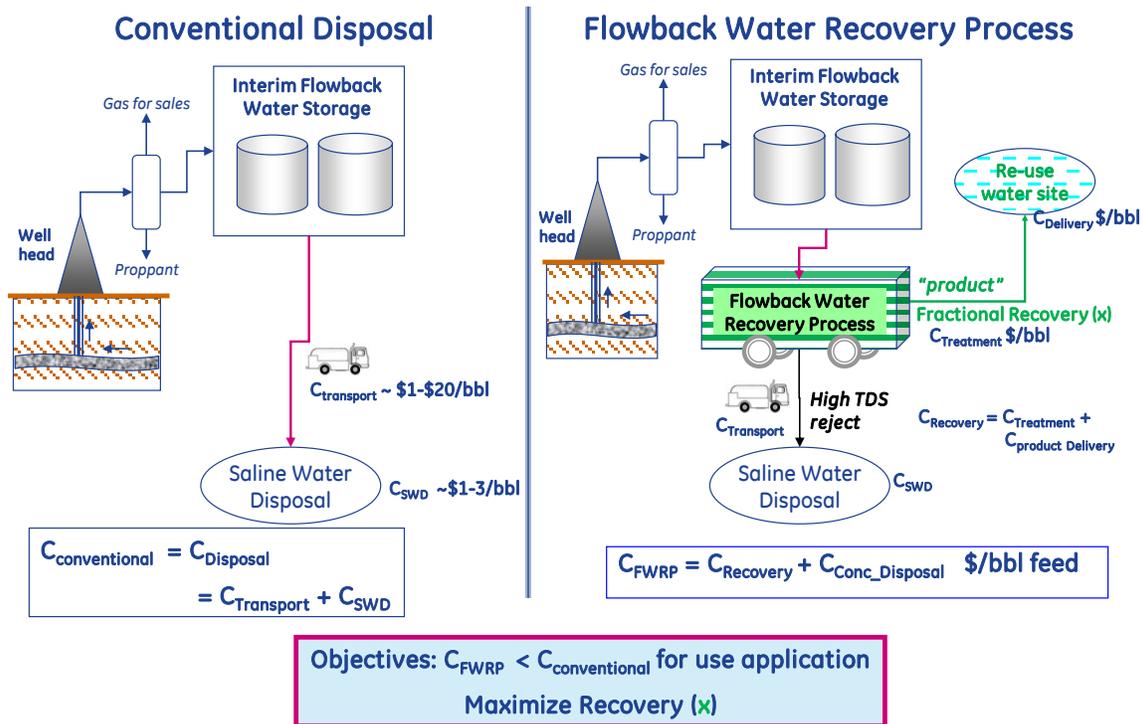


Figure 58. System configurations for the conventional frac flowback disposal via underground saline water disposal and the Flowback Water Recovery Process 50-gpm mobile rig under consideration in this project.

For this project we have considered the main driver for an FWRP to be **financial** and hence the key economic criterion at any frac flowback site is assumed to be:

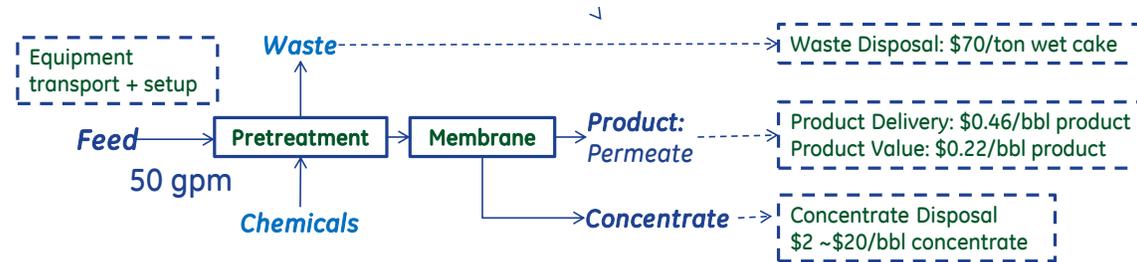
$$C_{FWRP} < C_{Conventional\ Disposal}$$

However, it is likely that other non-economic drivers, such as regulatory mandates or public relations may also induce the producer to opt for the FWRP. In those cases, the objective may be to minimize  $C_{FWRP}$ .

### 3.6.2 Membrane Desalination Mobile Rig – FWRP costs & economical “cut-off” TDS

The cost correlations and parameters of interest were discussed in Section 3.2.12 and are summarized in Figure 59.

## Cost correlations for mobile 50 gpm membrane rigs



$$\text{Recovery, } X = \text{Product/Feed}$$

$$C_{\text{Recovery}} = (C_{\text{Setup}} + C_{\text{Pretreatment}} + C_{\text{Membrane}} + C_{\text{Chemicals}} + C_{\text{Waste}}) + (C_{\text{Product Delivery}} - C_{\text{product Value}}) * X$$

$$C_{\text{Conc\_Disposal}} = C_{\text{Disposal}} * (1-X)$$

$$C_{FWRP} = C_{\text{Recovery}} + C_{\text{Conc\_Disposal}} \quad \$/\text{bbl feed}$$

$$C_{\text{Disposal}} = C_{\text{Transportation}} + C_{\text{SalineWD}}$$

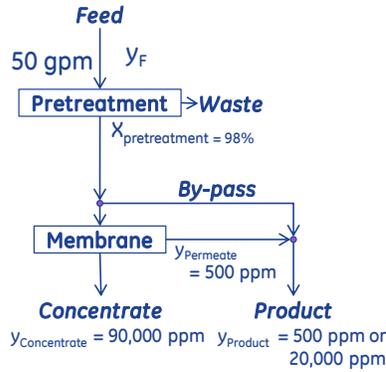
$$C_{\text{Conventional}} = C_{\text{Disposal}} \quad \$/\text{bbl feed}$$

Process Step	Cost parameters & units		
	\$/bbl feed	\$/bbl product	\$/bbl concentrate
Equipment setup	C_Equipment_setup		
Pretreatment	C_Pretreatment		
Chemicals	C_Chemicals		
Waste disposal	C_Waste		
Membrane process	C_Memb_fixed		
Product delivery		C_Product_delivery	
Product value		C_Product_value	
Concentrate disposal			C_Conc_disposal

Figure 59. Cost parameters, units and correlations for the FWRP & Conventional processes described in Figure 58.

The extent of water product recovery expected from a membrane-based desalination system using the pretreatment processes developed in this project is plotted as a function of the feed TDS concentrations in Figure 60. Note that due to the membrane system designs evaluated in Task 4, it is possible to extend the retentate concentration to 90,000 ppm TDS compared to 70,000 ppm TDS typically used in seawater desalination (cf. Figure 47), and thus achieve greater water recovery at the same feed TDS concentration. This is illustrated for the Product-4 quality (500 ppm TDS) in Figure 60.

## Membrane System: Water recovery for different product requirements



Water Recovery vs. Feed TDS concentration & operating conditions

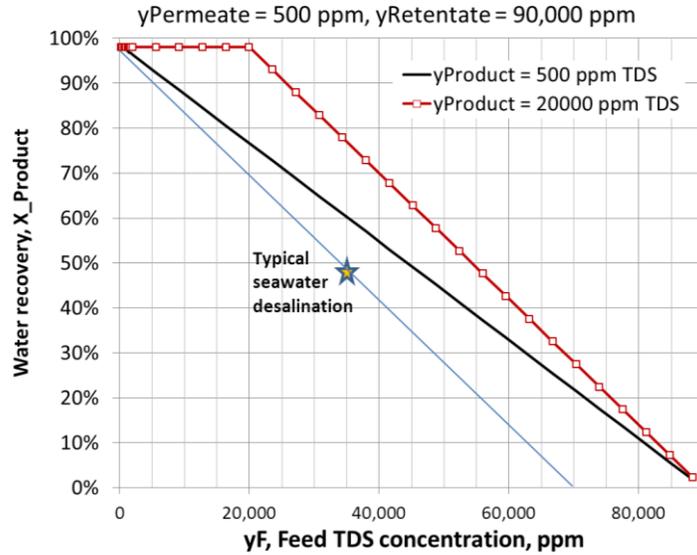


Figure 60. Mass balance profiles for membrane desalination based FWRP for Product-3 (20,000 ppm) and Product-4 (500 ppm).

Note typical seawater desalination operates at  $y_{\text{Retentate}} = 70\text{K}$  ppm TDS while choice of pretreatment & membrane system conditions for flowback recovery allow  $y_{\text{Retentate}} = 90\text{K}$  ppm TDS, and thus higher recovery.

For Product-3, where the desired product TDS is less stringent at  $<20,000$  ppm, we see much higher recoveries compared to Product-4. It is possible to achieve the Product-3 target by either:

- Alternative 1: Use high-flux low-rejection membranes that yield a permeate product with TDS  $<20,000$  ppm TDS (as originally conceived for this project) or
- Alternative 2: Use high-selectivity but lower flux membranes typically used for seawater desalination that yield a permeate product with TDS  $<500$  ppm and achieve the desired Product-3 target by blending with a by-passed portion of the feed to the membrane unit, as shown in Figure 60.

During the cost estimations for the membrane systems described in Section 3.2.12, we had observed that for such small throughput (50-gpm) configurations the overall cost was dominated by the balance of plant rather than the number of membrane modules and power consumption (cf. Figure 49). Hence, from a practical perspective, it is prudent to design the conceptual process to produce the most stringent product, i.e. 500 ppm permeate, and then blend appropriately to meet the less stringent product quality. In other words, we select the Alternative 2 described above.

The main cost components,  $C_{\text{Recovery}}$ ,  $C_{\text{Concentrate Disposal}}$  and the overall  $C_{\text{FWRP}}$  are illustrated for a membrane desalination mobile rig producing Product-4 quality (500 ppm TDS) in Figure 61. These costs are plotted as a function of  $y_F$ , the feed TDS concentration for an assumed value of  $C_{\text{Disposal}}$ . These values are normalized with respect to  $C_{\text{Conventional}}$ . Thus, all regions with  $C_{\text{FWRP}}/C_{\text{Conventional}} < 1$  would be economically attractive for FWRP.

We observe in Figure 61 that that  $C_{\text{Recovery}}$  decreases as  $y_F$  increases because the extent of water recovery,  $X$ , decreases with increasing  $y_F$  (cf. Figure 60), which results in lowering the contribution from product delivery costs. Interestingly, the slope of this decline is very small with increasing  $y_F$  because the recovery costs are dominated by the Treatment Cost components.

The  $C_{\text{Concentrate Disposal}}$  increases as  $y_F$  increases (and recovery decreases). The increase in  $C_{\text{Concentrate Disposal}}$  is much sharper because  $C_{\text{Disposal}}$  is usually much higher than  $C_{\text{Product delivery}}$ . The net effect of the profiles of  $C_{\text{Recovery}}$  and  $C_{\text{Concentrate Disposal}}$  is that  $C_{\text{FWRP}}$  increases with  $y_F$ .

## Membrane Recovery: Cost vs. Feed TDS

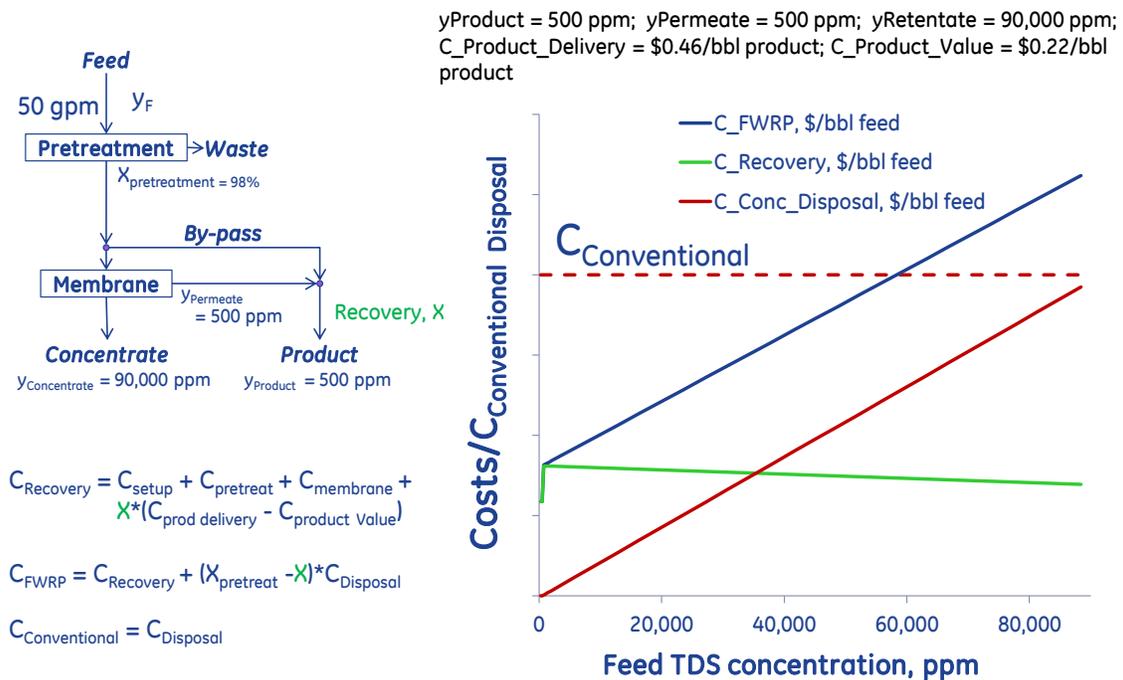


Figure 61. Cost components for the membrane-based FWRP:  $C_{\text{Recovery}}$ ,  $C_{\text{Conc\_disposal}}$  and  $C_{\text{FWRP}}$  for the operating and cost parameters developed in this project and for an assumed value of  $C_{\text{Disposal}}$ .

*Definition of economical "Cut-off" TDS for frac re-use: The value of  $y_F$  where the  $C_{\text{FWRP}}$  crosses the  $C_{\text{Conventional}}$  line represents the economical "cut-off" TDS for that particular frac flowback site.*

In Figure 62, the  $C_{FWRP}$  for membrane-based desalination mobile rig for producing Product-3 (20,000 ppm TDS) is compared to that for Product-4 (500 ppm) (previously illustrated in Figure 61). We observe that the “cut-off” TDS in this particular case is  $y_F = 58,000$  ppm TDS for Product-4 and  $y_F = 65,000$  ppm TDS for Product-3; the water recovery is 35% in both cases (cf. Figure 60).

## Membrane Recovery: Cost sensitivity to product TDS requirements

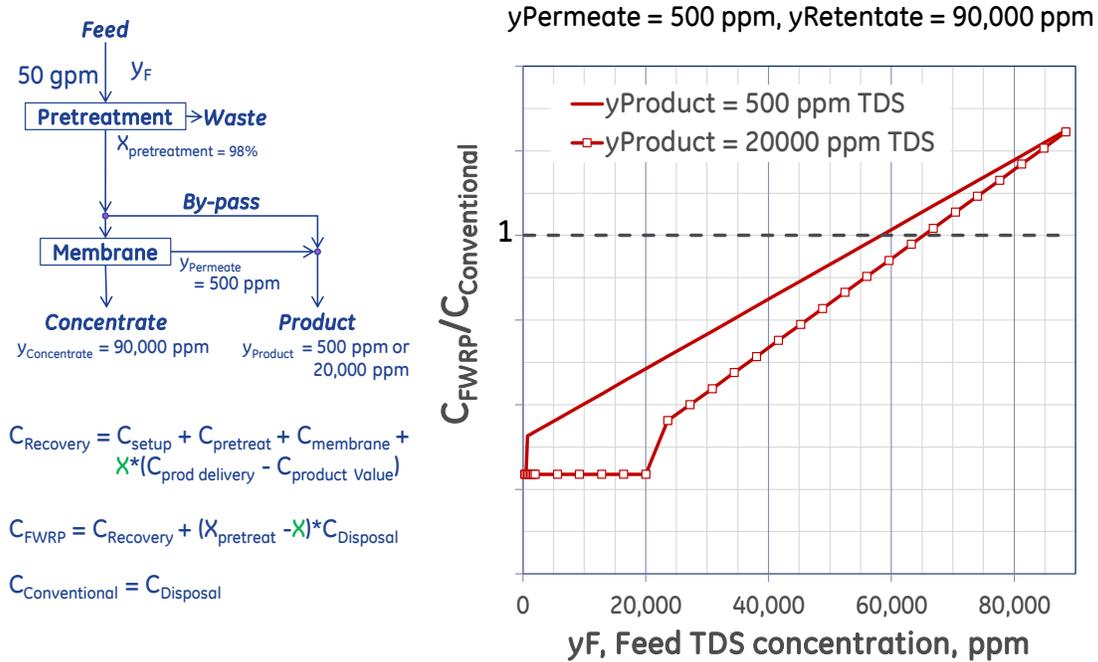
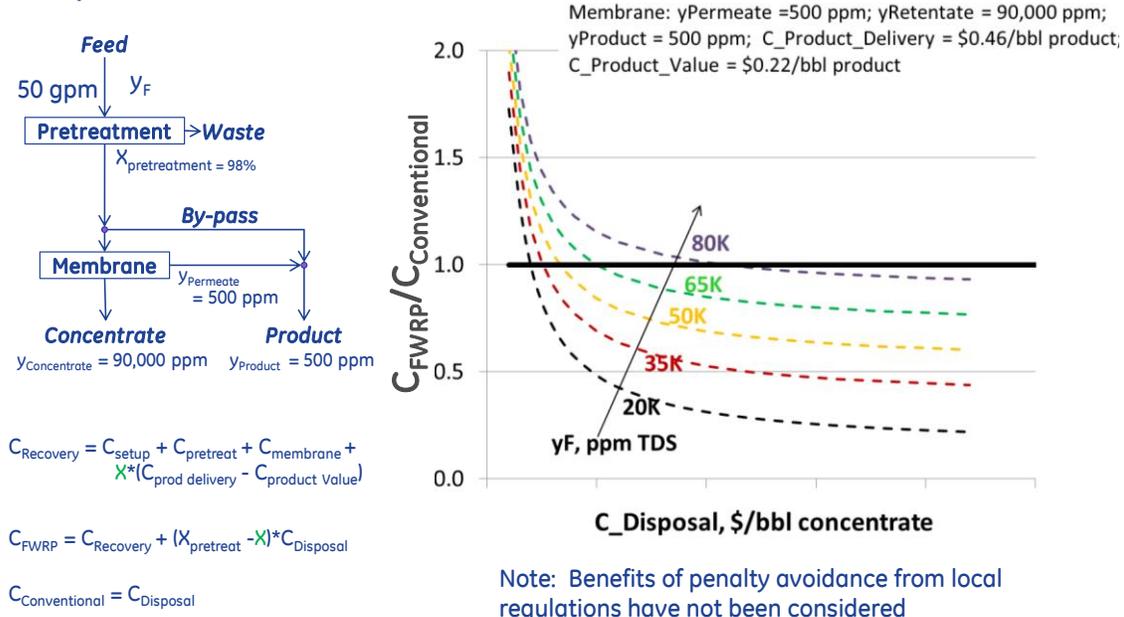


Figure 62. Cost of membrane-based FWRP vs. feed TDS concentrations for Product-3 and Product-4 quality specifications.

This “cut-off” TDS is a strong function of the  $C_{Disposal}$ , the cost of transport and disposal of the saline water in Class II disposal wells. This is illustrated in Figure 63 for a membrane desalination mobile rig producing Product-4 quality (500 ppm TDS) where the  $C_{FWRP}/C_{Conventional\ Disposal}$  ratio is plotted as a function of varying  $C_{Disposal}$  at different values of  $y_F$ . The points where the curves intersect the solid black line representing  $C_{FWRP}/C_{Conventional\ Disposal} = 1$  represent the “cut-off” TDS at the  $y_F$  and  $C_{Disposal}$  values prevalent at the frac flowback disposal site under consideration.

## Membrane System: Cost sensitivity to concentrate disposal costs



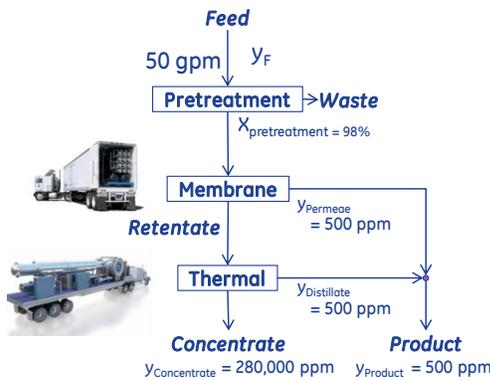
Economic benefits of FWRP highly dependent on saline water disposal costs at shale plays

Figure 63. Profiles for  $C_{\text{FWRP}}/C_{\text{Conventional}}$  for the membrane system vs. Concentrate disposal costs at varying feed TDS concentrations.

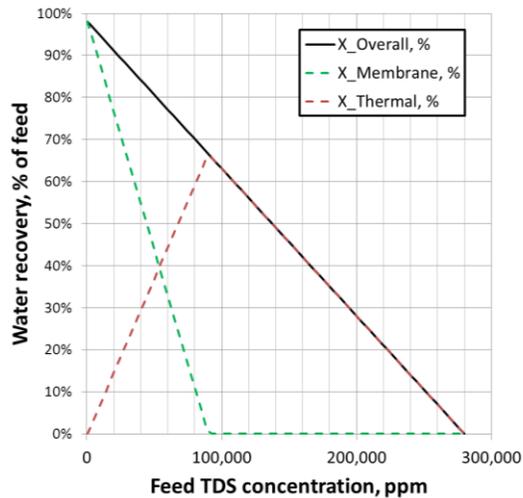
### 3.6.3 Hybrid Membrane+Thermal Mobile system – FWRP costs & economical “cut-off” TDS

The extent of water recovery in the membrane desalination system is limited by the retentate concentration, as described earlier. Further water recovery from the retentate is possible via thermal desalination. This is illustrated in Figure 64 where a hybrid mobile system is considered for a Product-4 quality (500 ppm TDS). The frac flowback stream is first pretreated and then sent through a membrane desalination rig to produce a 500ppm permeate product. The retentate with 90,000 ppm TDS is then distilled in a mobile evaporator (such as that introduced by GE Water<sup>22</sup> recently) to obtain distillate with <500 ppm TDS and a concentrate with 280,000 ppm TDS. As seen in Figure 64, such a configuration yields much higher recovery than the membrane system alone. For example, for a feed with  $y_F = 35,000$  ppm TDS, the hybrid system yields 85% recovery vs. 61% for the membrane rig alone.

# Hybrid Membrane + Thermal Recovery: Water recovery



Hybrid Membrane + Thermal process: Water recovery vs. Feed TDS



Hybrid yields much higher water recovery than membrane alone.

Figure 64. Hybrid system incorporating pretreatment, membrane desalination and thermal distillation to yield Product-4 quality (500 ppm TDS); the 90K ppm TDS retentate from the membrane unit is distilled in the mobile evaporator to yield a 280,000 ppm TDS concentrate.

Of course, the capital and operating costs for this hybrid system would be greater than the membrane system alone. Hence, the  $C_{FWRP}$  for the overall hybrid system will have to be considered. This is illustrated in Figure 65, where the  $C_{FWRP}$  is plotted as a function of feed TDS,  $y_F$  for the Membrane system only, Thermal (Evaporator) system only and Hybrid Membrane + Thermal system. For the assumed  $C_{Disposal}$  value in Figure 65, the Membrane system is cheaper than either of the other systems when the feed TDS concentrations are low (<35,000 ppm TDS in this case). The economical “cut-off” TDS for the Hybrid case is higher at 82,000 ppm TDS compared to 68,000 ppm TDS for Membrane system alone. More importantly, at these “cut-off” TDS values, the water recovery is much higher at 69% for the Hybrid case vs. 28% for the Membrane alone (cf. Figure 64).

## Hybrid Membrane + Thermal Recovery: Cost comparisons

$y_{\text{Product}} = 500 \text{ ppm}$ ;  $y_{\text{Permeate}} = 500 \text{ ppm}$ ;  $y_{\text{Retentate}} = 90,000 \text{ ppm}$ ;  
 $y_{\text{Distillate}} = 500 \text{ ppm}$ ;  $y_{\text{Concentrate}} = 280,000 \text{ ppm}$   
 $C_{\text{Product\_Delivery}} = \$0.46/\text{bbl product}$ ;  $C_{\text{Product\_Value}} = \$0.22/\text{bbl product}$

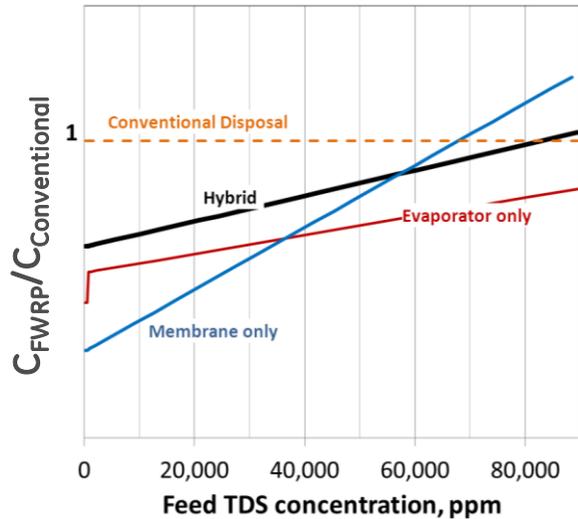
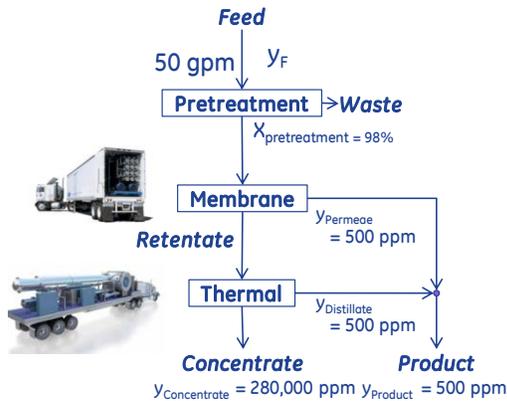


Figure 65. Cost profiles for the Membrane system alone, Mobile evaporator alone and the Hybrid membrane+thermal systems as a function of feed TDS concentration.

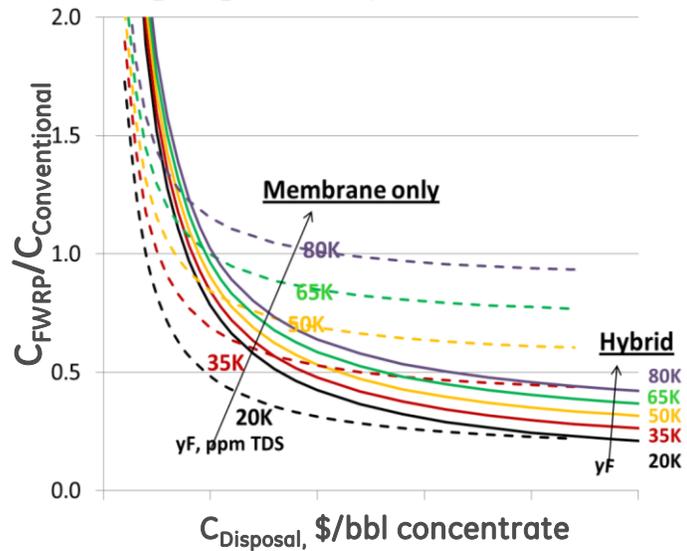
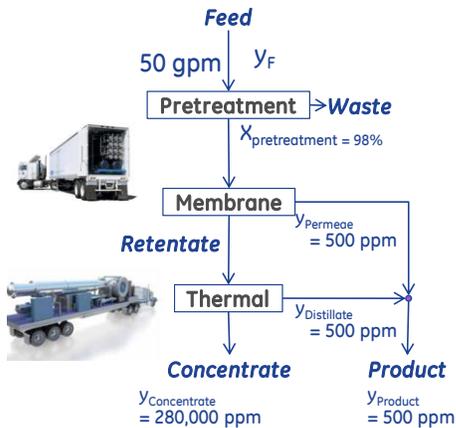
Again, as discussed earlier for the membrane mobile rig in Section 3.6.3, the economical “cut-off” TDS is a strong function of the local  $C_{\text{Disposal}}$  prevalent at the frac flowback site. For the Hybrid system the  $C_{\text{FWRP}}/C_{\text{Conventional Disposal}}$  ratio is plotted as a function of varying  $C_{\text{Disposal}}$  at different values of  $y_F$  in Figure 66. The curves for the Hybrid case are compared with those for the Membrane alone (cf. Figure 63).

We observe the following in Figure 66:

- The curves at the different values of  $y_F$  for the Hybrid case are much closer than for the Membrane case alone due to the increased recovery for the Hybrid case
- The Membrane alone case is more economical for the lower  $C_{\text{Disposal}}$  cases mainly due to the lower overall capital costs vs. the Hybrid case. However, the Hybrid case becomes more economically attractive as the  $C_{\text{Disposal}}$  rises.

# Hybrid Membrane + Thermal Recovery: Cost comparisons

Membrane:  $y_{Permeate} = 500$  ppm;  $y_{Retentate} = 90,000$  ppm;  
 Thermal:  $y_{Distillate} = 500$  ppm;  $y_{Concentrate} = 280,000$  ppm;  
 Hybrid:  $y_{Product} = 500$  ppm;  $C_{Product\_Delivery} = \$0.46/\text{bbl product}$ ;  
 $C_{Product\_Value} = \$0.22/\text{bbl product}$



Membrane alone more economical for low disposal cost plays  
 Hybrid more economical at higher disposal cost plays

Figure 66. Profiles for  $C_{FWRP}/C_{Conventional}$  ratio vs Concentrate disposal costs for varying feed TDS concentrations.

## 4 Summary and Conclusions

- Frac flowback water is not a uniform “raw material” from a process development perspective:
  - Flowback rates decrease sharply from as high 50~150 bbl/hr for the first 5-10 days to <10 bbl/day beyond Day 30 of flowback.
  - Flowback composition varies considerably depending on the geological formation and operating conditions (e.g. chemicals introduced during the drilling and fracturing operations, diesel and compressor oils from pumps, etc.), and more importantly, as a function of time at the same well.
- Applicability of low-TDS (< 45,000 ppm) recovery approach is ~90-100% for Fayetteville and Woodford shales, while limited to very early flowback in Barnett, Marcellus and other shales.
- There is no clear consensus on product quality requirements for re-use in hydrofracturing. Based on feedback, 4 product options were identified, namely: Product-1 based on “Clarified only”, Product-2 based on “Softened only”, Product-3 based on “Desal to 20Kppm TDS” and Product-4 based on “Desal to <500ppm TDS”.
- Lab-scale experiments showed that the identified “pretreatment” techniques were successful in clarification and hardness-removal and able to meet the quality requirements for Product-1 and Product-2, and as pretreatment to the membrane desalination process.
- A novel GCxGC+ToFMS method for analysis of hydrocarbons was found useful in providing a qualitative understanding of the effect of pretreatment methods on the presence and disappearance of organic compounds in the treated frac flowback waters.
- RO membrane fouling experiments conducted using commercially available 2” diameter spiral wound RO modules with pretreated flowback water showed identical water-flux and salt-rejection profiles as the control solution (35K ppm TDS NaCl in deionized water). This indicated the effectiveness of the downselected pretreated conditions in removal of potential membrane foulants (inorganic salts and colloidal inorganic and organic compounds).
- For Product-3 and Product-4, that require desalination to TDS levels <20,000 ppm and <500 ppm, respectively, various membrane system configurations were evaluated and optimized via performance modeling with GE Winflows software to increase water product recovery. For a feed solution composition similar to that obtained after pretreating (lime softened and filtered) Site-2 Day-26 sample, membrane system configurations were identified that increased the recovery from 49% using the standard seawater-desalination design to as high as 61.5%. The maximum retentate concentration correspondingly increased from 68K ppm to 90K ppm TDS for these conditions. The increase in capital costs due to additional pumps, membrane modules, interconnected piping and controls for the new configuration was more than offset by the increased water recovery when the overall FWRP was considered.

- The estimated Treatment Costs for the four product options were within the cost criterion of < \$2/bbl flowback, in line with preliminary feedback on customer expectations. The cost estimations were based on reliable values obtained either from vendors or internal cost information for the desired equipment. Other cost factors, such as costs of electricity, type and cost of labor, and waste handling & disposal, were also obtained either from appropriate vendors or internal cost information.
- Membrane module and Electricity costs were only 2% and 5%, respectively, of overall operating costs for such small throughput (50 gpm) mobile rigs capable of producing Product-3 or Product-4. Nearly 75% of the operating costs are related to “fixed” charges (related to capital equipment and rig transportation & setup) while chemicals and solids waste disposal accounted for the remaining 18%.
- Costs of the modeled overall Flowback Water Recovery Process (FWRP) were compared to those for the conventional saline water disposal method. For the desired economic consideration of  $C_{FWRP}/C_{Conventional} \leq 1$  the “cut-off” feed TDS concentration would depend on the disposal costs prevalent at the frac flowback site. Higher disposal costs would make FWRP attractive as seen in the sensitivity plots of  $C_{FWRP}/C_{Conventional}$  vs.  $C_{Disposal}$  at different feed TDS concentrations. These charts thus provide a means of comparing the relative value of FWRP for a well flowback treatment opportunity based on prevailing disposal costs and anticipated flowback TDS levels.
- The Hybrid membrane + thermal approach, wherein a 50-gpm pretreatment & membrane desalination rig is followed by a mobile evaporator to treat the retentate from the membrane unit, provides much higher water recovery (e.g. 85% vs. 61% for Membrane alone for a feed containing 35,000 ppm TDS). However, the Hybrid process costs more than individual process options alone due to the high fixed costs for such small throughput (50 gpm) systems. The Membrane alone case is more economical for the lower  $C_{Disposal}$  cases mainly due to the lower overall capital costs vs. the Hybrid case. However, the Hybrid case becomes more economically attractive for the high  $C_{Disposal}$  shale plays where local SWD sites are unavailable, thus leading to higher flowback water transportation costs for the conventional disposal method.

Overall, based on bench-scale experiments on pretreatment and membrane desalination fouling conducted with typical frac flowback water samples from Woodford shale, membrane desalination system modeling, and cost analysis of the flowback water recovery process, we conclude:

- Technical Performance: There is a high level of confidence that the conceptual processes will be effective to yield the Products-1, -2, -3 and -4 of desired quality since these process flow schemes were constructed based on the bench-scale experimental studies on the individual separation technologies using actual frac flowback samples. Many of the initial concerns were mitigated by appropriate choice and verification of process operating conditions in the lab-scale experiments.

- **Cost Performance:** The estimated Treatment Costs for the four product options were within the cost criterion of < \$2/bbl in line with preliminary feedback on customer expectations. Using the  $C_{FWRP}/C_{Conventional} \leq 1$  as the desired economic criterion, for Product-4 (500 ppm TDS), the “cut-off” TDS for frac flowback water recovery is in the range of 20,000 ppm to 65,000 ppm depending on the local saline water disposal costs. The sensitivity plots of  $C_{FWRP}/C_{Conventional}$  vs.  $C_{Disposal}$  at different feed TDS concentrations provide a means of comparing the relative value of FWRP for a well flowback treatment opportunity based on prevailing disposal costs and anticipated flowback TDS levels.
- **Mobility Performance:** Based on vendor information on sizes and operations of the various equipment identified for the conceptual processes, and internal data on mobile rig operations, 50-gpm mobile rig configurations may be achievable for the four products under consideration.
- Hybrid membrane + thermal systems based on membrane desalination and a mobile evaporator may be attractive for treating Low-TDS frac flowback water for high disposal-cost plays.
- It is believed that the parametric value assessment tool approach developed in this project to assess overall economic attractiveness of any Flowback Water Recovery Process (FWRP) relative to conventional disposal, and thus relating sensitivity of water recovery via treatment processes employed and product/reject disposal costs, will provide a rational basis for treatment process selection appropriate to well flowback characteristics and local disposal costs & regulations.

## APPENDIX: Water Chemistry of Drilling and Hydrofracturing Fluids

### Drilling fluid

The drilling fluids used depend on the geology of the shale formation and the technology bias/experience of the operator. Most of the information is held proprietary and confidential. However, a good summary of the various components is provided at the DOE NETL website<sup>23</sup>. Information relevant to this project are reproduced below:

- Drilling fluids or muds are made up of a base fluid (water, diesel or mineral oil, or a synthetic compound), weighting agents (most frequently barium sulfate [barite] is used), bentonite clay to help remove cuttings from the well and to form a filter cake on the walls of the hole, lignosulfonates and lignites to keep the mud in a fluid state, and various additives that serve specific functions.
- Mud Additives: Water-based muds (WBMs) would be preferable because they are not only inexpensive but the used mud and cuttings from wells drilled with WBMs can be readily disposed of onsite at most onshore locations. However, for difficult drilling situations, such as wells drilled in reactive shales, deep wells, and horizontal and extended-reach wells, WBMs do not offer consistently good drilling performance. For these types of drilling situations at onshore sites, the industry relies primarily on oil-based muds (OBMs). OBMs perform well, but may be subject to more complicated disposal requirements for onshore wells. OBMs contain diesel or mineral oil as the base fluid and may be harmful to the environment if directly discharged to a water source.
- Synthetic-Based Muds (SBMs): These are nonaqueous fluids (other than oils) as their base. Examples of these base fluids included internal olefins, esters, linear alpha-olefins, poly alpha-olefins, and linear paraffins. SBMs share the desirable drilling properties of OBMs but are free of polynuclear aromatic hydrocarbons and have lower toxicity, faster biodegradability, and lower bioaccumulation potential. The EPA has identified this product substitution approach as an excellent example of pollution prevention that can be accomplished by the oil and gas industry. SBMs drill a cleaner hole than water-based muds, with less sloughing, and generate a lower volume of drill cuttings. In offshore drilling, SBMs are recycled to the extent possible, while WBMs are discharged to the sea.
- New Drilling Fluid Systems: Drilling fluid companies are developing variations of fluid systems that are much more amenable to biotreatment of the subsequent drilling wastes. It is likely that companies will continue to develop fluids with suitable drilling properties that contain fewer components or additives that would inhibit subsequent break down by earthworms or microbes. In some circumstances, the constituents of the muds could actually serve as a soil supplement or horticultural aid.

- Other developments in drilling fluids could lead to entirely different formulations. Drilling fluids based on formate brines have been suggested as being more environmentally friendly than traditional fluids. Formate brines are created by reacting formic acid with metal hydroxides. Common examples are cesium formate (HCOO-Cs+), potassium formate (HCOO-K+), and sodium formate (HCOO-Na+).

Alternate Weighting Agents: Substitution of some of the key components of drilling fluids with more environmentally friendly products could reduce mass loadings of potentially harmful substances to the environment. Barite is the most commonly used weighting agent. Other readily available weighting agents include hematite (Fe<sub>2</sub>O<sub>3</sub>) and calcium carbonate (CaCO<sub>3</sub>). Other wells have been drilled using ilmenite (FeTiO<sub>3</sub>) instead of barite as a weighting agent.

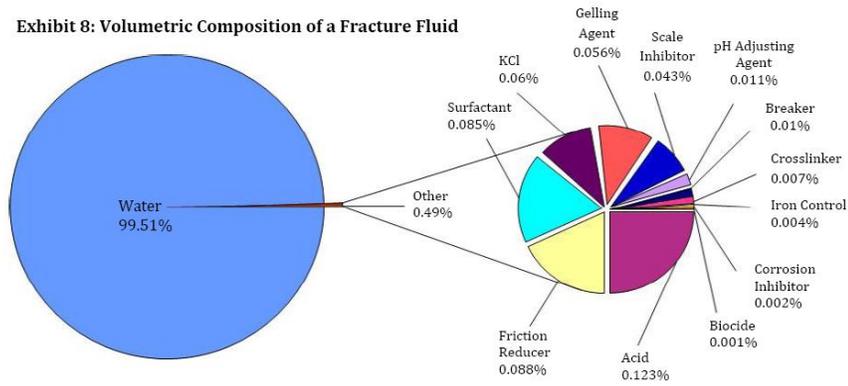
## Hydrofracturing Fluid

Hydraulic fracturing of gas shale reservoirs involves sequenced events requiring thousands of barrels of water-based fracturing fluids mixed with proppant materials pumped in a controlled and monitored manner into target shale formations above fracture pressure<sup>24</sup>. Fracturing fluids used for fracturing gas shales include a variety of additive components, each with an engineered purpose to facilitate fractures and the production of gas<sup>25</sup>. Currently, the trends in shale wells are water based or mixed slickwater-fracturing fluids. These are water-based fluids mixed with friction reducing additives<sup>26</sup>, which allows a fracturing fluid and proppant to be pumped to the target zone at a higher rate and reduced pressure than by using water alone. In addition to friction reducers, other additives including biocides are utilized to prevent micro-organism growth and to reduce bio-fouling of fractures. Oxygen scavengers and other stabilizers which prevent corrosion of metal pipes and acids which are used to remove drilling mud damage near the wellbore area are also common either in fracturing fluids or as part of fracture treatments.

An excellent review of the various components typically used during slickwater hydrofracturing is provided by D. Arthur et al of ALL Consulting<sup>25</sup> and are reproduced in Figures 18 and 19. Some of the operators have also published information on their practices, most notably, Chesapeake Energy<sup>27</sup>. Fortuna Energy, a subsidiary of Talisman Inc., has provided details on the amounts of chemicals used, and their effective concentrations in the fracturing fluid, as shown in Figure 20<sup>28</sup>.

From the flowback water treatment perspective, although it is expected that some or all of these additives may be expected in the flowback, no literature reports confirming the presence and concentrations of these additives could be found. It is likely that these compounds may get chemically, physically or microbiologically altered or destroyed during the hydrofracturing process or become lost in the shale formation. Although some of these additives, such as guar gel, polyacrylamides, petroleum distillates may affect membrane performance; the actual impact would only have to be experimentally determined with flowback water samples.

Exhibit 8: Volumetric Composition of a Fracture Fluid



Source: Compiled from Data collected at a Fayetteville Shale Fracture Stimulation by ALL Consulting 2008.

Figure 67. Volumetric composition of a representative hydraulic fracturing fluid excluding the proppants (reproduced from D. Arthur et al., ALL Consulting<sup>25</sup>).

EXHIBIT 9: FRACTURING FLUID ADDITIVES, MAIN COMPOUNDS AND COMMON USES.			
Additive Type	Main Compound	Use in Hydraulic Fracturing Fluids	Common Use of Main Compound
Acid	Hydrochloric acid or muriatic acid	For the fracturing of shale formations, acids are used to clean cement from casing perforations and drilling mud clogging natural formation porosity, if any prior to fracturing fluid injection (dilute acids concentrations are typically about 15% acid)	Swimming pool chemical and cleaner
Biocide	Glutaraldehyde	Fracture fluids typically contain gels which are organic and can therefore provide a medium for bacterial growth. Bacteria can break down the gelling agent reducing its viscosity and ability to carry proppant. Biocides are added to the mixing tanks with the gelling agents to kill these bacteria.	Cold sterilant in health care industry
Breaker	Sodium Chloride	Chemicals that are typically introduced toward the later sequences of a frac job to "break down" the viscosity of the gelling agent to better release the proppant from the fluid as well as enhance the recovery or "flowback" of the fracturing fluid.	Sodium chloride is also used as a food preservative.
Corrosion inhibitor	N,N-dimethyl formamide	Used in fracture fluids that contain acids; inhibits the corrosion of steel tubing, well casings, tools, and tanks.	Used as a crystallization medium in Pharmaceutical Industry
Crosslinker	Borate Salts	There are two basic types of gels that are used in fracturing fluids; linear and cross-linked gels. Cross-linked gels have the advantage of higher viscosities that do not break down quickly.	Non-CCA wood preservatives and fungicides
Friction Reducer	Petroleum distillate or Mineral oil	Minimizes friction allowing fracture fluids to be injected at optimum rates and pressures	Cosmetics including hair, make-up, nail and skin products
Gel	Guar gum or hydroxyethyl cellulose	Gels are used in fracturing fluids to increase fluid viscosity allowing it to carry more proppant than a straight water solution. In general, gelling agents are biodegradable.	Guar gum is a food-grade product used to increase the viscosity and elasticity of foods such as ice cream, and salad dressings
Iron Control	Citric acid	Sequestering agent that prevents precipitation of metal oxides.	Citric Acid it is used to remove lime deposits. Lemon Juice is approximately 7% Citric Acid
KCl	Potassium Chloride	Added to water to create a brine carrier fluid.	Low sodium table salt substitute
Oxygen scavenger	Ammonium bisulfite	Oxygen present in fracturing fluids through dissolution of air causes the premature degradation of the fracturing fluid, oxygen scavengers are commonly used bind the oxygen.	Used in cosmetics
Proppant	Silica, quartz sand	Proppants consist of granular material, such as sand, which is mixed with the fracture fluid and is used to hold open the hydraulic fractures allowing the gas or oil to flow to the production well.	Play box sand, concrete or mortar sand
Scale inhibitor	Ethylene glycol	Additive to prevent precipitation of scale (calcium carbonate precipitate).	Automotive antifreeze and de-icing agent
Surfactant	Naphthalene	Used to increase the viscosity of the fracture fluid.	Household fumigant (found in mothballs)

Figure 68. Additives in the hydrofracturing fluid (reproduced from D. Arthur et al, ALL Consulting<sup>3</sup>)

<b><i>Universal Product</i></b>	<b><i>Loading</i></b>	<b><i>Density</i></b>	<b><i>Components</i></b>	<b><i>% Range</i></b>	<b><i>wt% in frac fluid</i></b>
<b>FRP-121</b>	5#pt		Anionic Polyacrylamide	98-100%	0.06%
<b>EC6116A</b>	0.25 gpt	10.4	Dibromoacetonitrile	1-5%	0.00156%
			2,2- Dibromo -3- nitrilopropionamide	10-30%	0.00935%
			Polyethylene Glycol	30-60%	0.01871%
<b>Flomax 70</b>	1 gpt	7.76	Methanol		0.085%
			Surfactant		0.085%
<b>Scalehib 100</b>	0.1 gpt	9.8	Ethylene Glycol	30-60%	0.00705%
			Polyacrylate		0.009%

Figure 69. Additives used in the hydrofracturing fluid, as reproduced from information published by Talisman Energy, Inc<sup>28</sup>

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