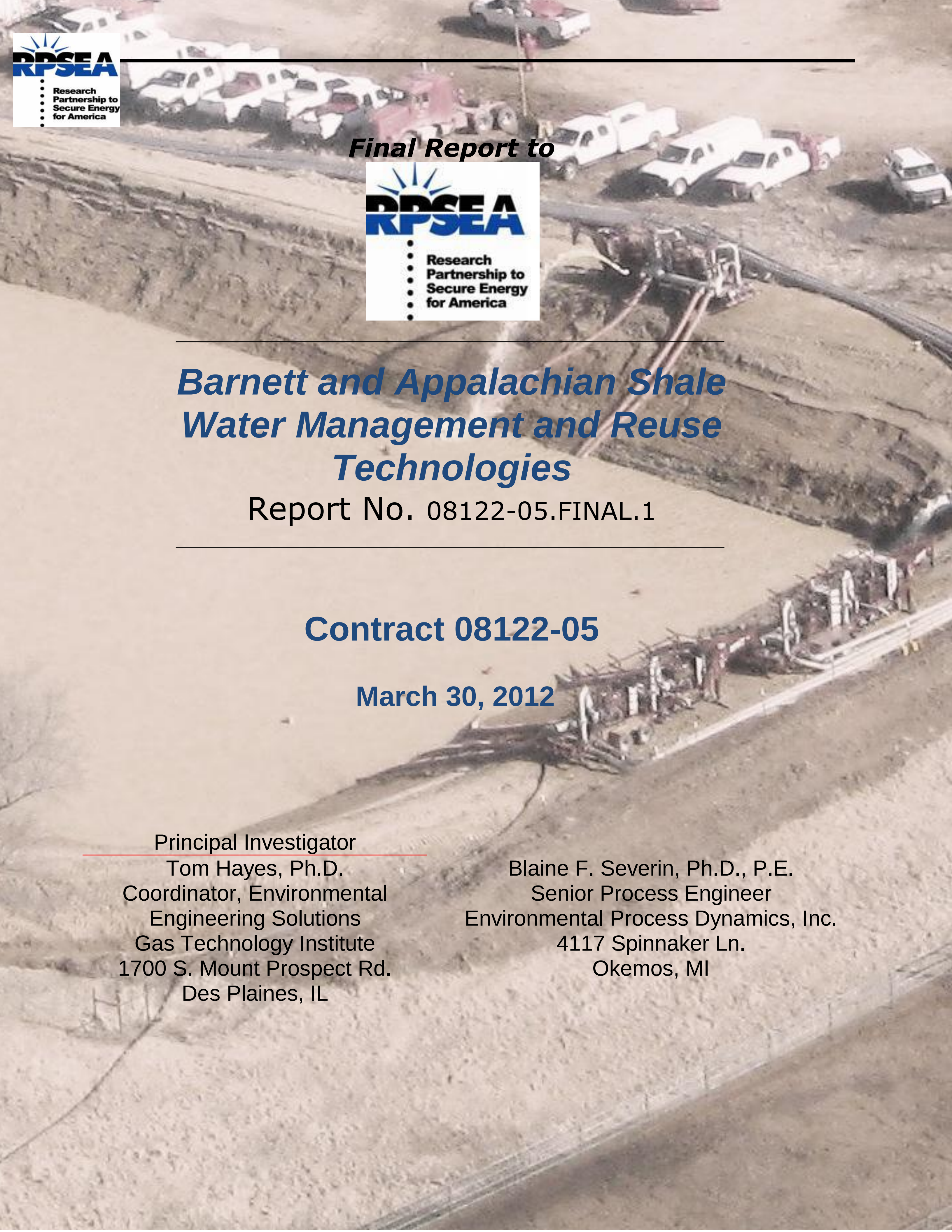

Final Report to

Barnett and Appalachian Shale Water Management and Reuse Technologies

Report No. 08122-05.FINAL.1

Contract 08122-05

March 30, 2012

Principal Investigator
Tom Hayes, Ph.D.
Coordinator, Environmental Engineering Solutions
Gas Technology Institute
1700 S. Mount Prospect Rd.
Des Plaines, IL

Blaine F. Severin, Ph.D., P.E.
Senior Process Engineer
Environmental Process Dynamics, Inc.
4117 Spinnaker Ln.
Okemos, MI

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Principal Investigator Signature Page

Thomas D. Hayes, Ph.D., Gas Technology Institute, Des Plaines, IL

March 30, 2012

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Abstract

During the fracture process, between 1 and 5 million gallons of water and sand is expended "down hole" into each extraction well to aide in the fracture. A portion of this water is recovered during the initial extraction of the gas. With proper management, recovered flowback water can represent a significant resource. Conversely, flowback water can represent a costly disposal problem. The nature of the chemistry and dynamics of recovered flowback water is of vital interest for effective environmental stewardship of a gas field. The objectives of this report are to better understand the chemical character of flowback water, its treatability, and long term sustainability issues associated with flowback water management.

This project approaches flowback water management at shale gas sites from several distinct levels, from broad management issues, to testing of potential treatment technologies, to full-scale verification of a commercially available technology. Alternative water sources and treatment options are presented to reduce impact and provide potential cost savings. The scientific, engineering, and economic data presented in this report may be used to form the basis of rational engineering and sustainability management tools. This final report summarizes these findings, with references to more detailed topical reports and (publication ready) papers that will be available from the RFSEA website.

Perhaps the broadest findings of this project are presented in the final task, Task 11; Preliminary Engineering Systems Analysis of Shale Gas Water Management, in which the water collection and salt generation at a hypothetical Marcellus gas play with 16 wells per field and 300 fields (4,800 wells) is projected for a period of 45 years into the future. In the early years of the play (its youth), the active fracture of new wells provides ample opportunity for the reuse of recovered flowback water within the play. As rates of fracturing of new wells and the refracturing of existing wells decline, the play enters middle age (first cross-over year) and the planned recovery volume exceeds the planned reuse volume. Segregation and pre-treatment of recovered water is at a premium. At some more future time, the rate of collection of produced water exceeds the rate of reuse (second cross-over) and the play is in old age. Water treatment and waste disposal become over-arching management issues. These findings put the remaining chapters into the perspective of these management needs.

Chapter 4 investigates the chemistry of 19 flowback events in the Marcellus and 5 flowback events in the Barnett. These data suggest that the organic nature of the flowback water is very similar to produced water from oil wells. Heavy metals are not an issue. The major disposal issue appears to be inorganic scale formers. The initial 30% of the recovered water is much less salty than the final 70%, suggesting that one viable option for management of these waters is simple segregation (Chapter 5). Treatment of mid-range waters (TDS 10,000-60,000 mg/l) with advanced innovative reverse osmosis membrane technology is investigated in Chapters 9-10 and with enhanced electrodialysis in Chapter 8. The treatment of heavy brine (60,000-100,000 mg/l) with distillation (mechanical vapor recompression) is verified in a report on a full-scale facility in the Barnett (Chapter 7). Alternate water sources in the Barnett are examined in Chapter 6.

Executive Summary

The Hydrofracking of shale for the development of natural gas sources has such great potential that it is often touted as an energy revolution. Good water management is essential to the economic sustainability of the industry.   The purpose of this project was to address water management issues by elucidating the chemical nature, and treatability of flowback waters, and to help develop sustainable water management plans.

Task 4: Water Characterization: This report covers recent sampling of flowback water from 19 sites in the Marcellus region and 5 sites from the Barnett. The database includes flowback rates, volumes, and chemical analyses of the injected water and the recovered flowback water. Chemical analyses include general chemical information typically used for drinking water analyses. The waters were tested for 70 volatile organics, 116 semi-volatile organics, 22 pesticides, PCB's, and 27 metals. The main salt composition appears to be sodium chloride. Chloride accounts for more than 93% of the anionic content. Some sulfate (500-1000 ppm range) is present in the Barnett samples, but is very low in the Marcellus samples (<100 ppm). Carbonate alkalinity, is quite low (<150 ppm). The commonly observed cations are sodium, calcium, barium, strontium, and iron. Heavy metals (other than iron) are generally either not detected, or in very trace concentrations.   The aromatics such as benzene, toluene, ethyl benzene, and toluene (BTEX) and other organic compounds, such as naphthalene, that are commonly associated with petroleum sites tend to be present only in low to trace concentrations (µg/l to mg/l). Heavier poly aromatic compounds (PAH's) such as commonly seen in petroleum wastewater are generally not present in the flowback water, and occur occasionally in only very trace concentrations.   Compounds that originate from human sources, such as pyridine and phthalate esters, are found in less than 50% of the samples. Methylated phenols are more commonly encountered, but only in concentrations between 10 to 100 ppb. Halogenated compounds are rarely encountered. Most of the organic chemical analyses performed resulted in "non-detects."

Task 5: Feasibility of Capture of Early Flowback Waters: Flowback waters from eleven shale gas well completions in the Barnett Shale were characterized for cumulative volume, electrical conductivity and selected constituents of interest (inorganic salts) as a function of time. Approximately one third of the fracwater used for a typical Barnett Shale well is recovered from the initiation of blowback until the time that the well produces salable volumes of natural gas. It was found at the field scale that a substantial portion of recovered flowback could be recycled for subsequent well completions across a wide range of TDS reuse thresholds. This finding stems from the observations that: 1) Only a portion (roughly a third) of the fracwater used to complete a well is typically recovered as flowback during the first several weeks following well completion, and 2) The volume–weighted TDS concentration is low enough so that the recovered flowback can be diluted for effective reuse. Thus, the substantial recovery of a useful fraction of flowback water for reuse is technically feasible and logistically achievable. The primary benefits of recycling flowback water include a potentially substantial reduction in the volume of freshwater needed to complete future wells as well as a concomitant reduction in the volume of wastewater that must otherwise be disposed. Empirical models describing flow rates and salt concentration are developed.

Task 6: Alternative Water Sources: The study investigates alternative sources of water to be used in the last completion phase (so-called “fracing”) of gas wells in the Barnett Shale play. It focuses on more rural counties (Montague, Jack, Palo Pinto, Parker, Erath, Hood, Somervell, Bosque, and Hill) located to the west of the core area (Denton, Johnson, Tarrant, and Wise Counties) where the Trinity aquifer is thin or absent. As gas production moves away from the core area toward the north, south, and west to access the remainder of the play, gas operators are faced with two challenges: (1) increased water scarcity and (2) measured reluctance to impact domestic and public water supplies. The study analyzes three sources with the potential to meet those goals: (1) treated wastewater outfalls from waste water treatment plants; (2) small water bodies outside the State regulation of surface water, and (3) smallish groundwater aquifers in Paleozoic-age disconnected sand bodies west of the more plentiful Trinity aquifer. An Arc-GIS tool was developed to determine the amount of water available at any point of the study area from the three characterized water sources within a given radius (note that water might be available too from more common sources such as large reservoirs). They were chosen at 5, 10, and 15 miles. To understand the adequacy of the resource, ~1000 points were selected on a regular grid covering the area of interest and statistics on water availability were then derived. To allow for comparison of water availability all sources use the same reference unit of million gallons per month. Results suggest that, assuming a dense development of the gas resource, in most cases, enough water is theoretically available on average (~40 million gallons available vs. ~10 million gallons used per month in a 5-mile radius). However, more than half of the total is surface water making it very susceptible to droughts. Droughts will do more than drying up the surface water resource, it will also limit access to treated waste water and groundwater as conservation takes place and as more users rely on groundwater, respectively. From an economic standpoint all the alternative sources described in the study are very fragmented leading to a diffuse ownership and a likely expensive water gathering system.

Task 7: Mechanical Vapor Recompression: This report presents process data on a full-scale (6,000-6,800 bbl/day) mechanical vapor recompression distillation (MVR) processing plant treating shale gas hydro-fracture flowback and produced water in North Central Texas (Barnett shale region). Process data were collected during a 60 day period. The pretreatment at this plant included caustic addition and clarification for total suspended solids and iron control. Pretreated water was distilled with three Aqua Pure MVR units, each rated at 2,000-2500 bbl/day. Distilled water recovery averaged 72.5% of the influent to the MVR’s. The influent total dissolved solids (TDS) fed to the MVR’s averaged just under 50,000 mg/l. More than 97.5% of the TDS was captured in the concentrate stream. The distillate averaged less than 1,900 mg/l TDS. The overall treatment (entire facility) required 72 SFC per barrel treated, or 100 SCF per barrel distillate produced. Fountain Quail estimates that recycling must be simple, rugged, proven and cost-effective. ROVER treatment (suspended solids removal only) is generally <$1/bbl and NOMAD treatment (MVR technology) can be from $3-$5/bbl, including labor, chemicals and equipment.

Task 8: Evaluation of Electrodialysis for Desalination of Flowback Waters: The treatment of flowback waters from shale gas hydrofracture with electrodialysis represented a dual technical challenge. Normal operation of electrodialysis is in the range of several thousand mg/l TDS and limited to several hundred mg/l calcium and magnesium. A number of problems were encountered that were systematically addressed as the project proceeded from the treatment of water containing pure sodium chloride (30,000-60,000 mg/l) to the treatment of solutions with sodium, calcium (up to 4,000 mg/l), barium (up to 400 mg/l), iron (up to 50 mg/l), and magnesium (up to 600 mg/l), and finally to the treatment of field samples from the Barnett and the Marcellus. A series of improvements and process recommendations are presented. The implementation of electrodialysis into an engineered water reuse systems appears economically feasible with and estimated cost of about $1 per barrel for water at 50,000 mg/l treated to a target of 10,000 mg/l. This compares beneficially to other competing costs, such as transportation, disposal, or advanced treatment such as mechanical vapor recompression.

Task 9: Development of Advanced Membrane Coatings: Reverse osmosis, nanofiltration, and ultrafiltration processes are potentially useful technologies for the desalination of flowback waters. The challenge in using membrane technology for produced water purification lies in fouling. Fouling is the build-up of particulate matter on the membrane either externally or internally which eventually inhibits its activity. Unlike regular seawater or brackish water, produced water contains many particulates, such as emulsified oils and organics, which aggressively foul the membrane. Polydopamine (PDOPA) was found to be an effective anti-fouling surface coating for UF, NF, and RO membranes for produced water purification. The deposition of PDOPA improved the permeate flux for all types of membranes studied during simulated oil/water emulsion filtration. For UF membranes, additional grafting by using poly(ethylene glycol) (PEG) further enhanced the fouling resistance. Energy savings were estimated for the PDOPA-modified UF and RO membranes in oil/water emulsion filtration by comparing power required per permeate volume. With the same amount of energy provided by the pump, the modified RO membrane produced 1.27 times more permeate volume than unmodified RO membrane after 1 hour oil/water emulsion filtration. The modified UF membrane permeate volume increased by a factor of 2.35 after 1 hour of oil/water emulsion filtration. By translating these benefits for industrial membrane applications, PDOPA modification is estimated to provide savings for 30% of the capital and 40-80% of the operating costs.

Task 10: Field Evaluation of Advanced Membrane Coatings: A 30 day field test of Anti-fouling Polymeric Membrane Coatings (developed at the University of Texas at Austin and licensed and marketed by Advanced Hydro, Inc.) was performed on shale flow-back “frac” produced water. Flow-back water collected from various shale wells in the Barnett Shale area was processed with ultra-filtration (UF) and reverse osmosis (RO) membranes. Membranes coated with polydopamine and PEG-amine were tested for their resistance to fouling due to organic and inorganic foulants in the feed water. Non-coated membranes were used as control for performance comparison. Poly-vinylidene Fluoride **(**PVDF) based spiral wound flat-sheet and polyacrylo nitrile (PAN) based outside-in hollow-fiber UF membranes were used in this pilot for pre-filtration for feed water prior to desalination using Polyamide RO membranes. Coated hollow-fiber UF elements outperformed non-coated elements, in terms of better cleaning efficacy (recovery) and higher flux, by almost 50%. In addition, coated spiral wound UF elements were easily maintained with daily chemical enhanced clean and fully recovered with regular acid-base cleaning operation. The coated spiral elements achieved 106 hours run time without using a strong oxidant. The autopsy study revealed that UF membranes were fouled with organic substances, which could be mainly removed by acid/base clean. No significant flux loss was observed for both coated and non-coated seawater RO membranes during the pilot. Coated RO membrane demonstrated much better salt rejection than non-coated under high salinity conditions. This brief project provided validation of the coatings technology and its benefit for produced water purification. In addition, with improved salt rejection during desalination, a two stage nanofiltration or nano/RO membrane system with an optimized ultra-filtration (UF) or micro-filtration (MF) membrane is expected to enable membrane based purification of produced water while maximizing water productivity and minimizing maintenance and energy costs.

Task 11: Systems Engineering and Life Cycle Analysis: The objective of this task was to better understand the chemical and hydraulic character of flowback water generated during the fracture of shale formations, and how these may influence the planning of gas generation facilities over a forty five year life cycle of individual wells, fields of wells, and plays of multiple fields. Data collected at 19 wells in the Marcellus shale were analyzed for total salt production, flowback rates, and extrapolations for long term water recovery. The median Marcellus event was used to interpret water recovery during the expected life of a projected play based on the particular needs of gas generation in the Marcellus. A Microsoft Excel Visual-Basic systems model was developed to incorporate a range of operating criteria on the projected life-cycle of the play. The core model tracks up to 32 wells per field at up to 350 fields per play. Concentrations and flow may be simulated by any reasonable set of parameters, such as the median Marcellus event. The projections are made on a daily basis for up to 45 years from the first completion. The variables include, but are not limited to, individual closure dates, number of wells per field, number of wells per field, number of refractures, installation rate, mobilization rate, days between refracture, number of drilling rigs mobilized, and recovered water rate. The analyses show that there are three distinct periods in the life of a play; young age, middle age, and old age. The water flow and salt generation during each period will likely dictate a different water management strategy for each period. The magnitude of water and salt generation is exceedingly high and early planning for each period in the life of the play is recommended.

List of Acronyms and Abbreviations

Acronym	***Definition***
AF	*Acre-foot = 325,850 gallons*
ASWCMC	*Appalachian Shale Water Conservation and Management Coalition*
BBL or bbl	*Barrel (42 gallons)*
BCF	*Billion Cubic Feet*
BSWCMC	*Barnett Shale Water Conservation and Management Committee*
BTEX	*Benzene, Toluene, Ethylbenzene, Xylenes*
C_0	*Concentration at well head (mg/l)*
C_{avg}	*Average impoundment concentration (mg/l)*
C_S	*Brine concentration in the groundwater (mg/l)*
C_W	*Wwell head concentration (mg/l)*
Flowback Water	*Water recovered in the weeks following hydraulic fracture*
Frac	*Hydraulic Fracture*
Frac Job	*Well completion event involving hydraulic fracturing*
FSAP	*Field Sampling and Analysis Plan*
F_X	*0.00035 conversion factor (mg/l x* F_X *= pounds/barrel)*
GAM	*Groundwater Availability Model*
k_1	*First order rate coefficient (*days^{-1}*)*
KDa	*Kilo-Darcy, Unit of Permeability*
M	*Mass of salt (lb) recovered between* $V_R = V_1$ *to* V_2
MWCO	*Molecular Weight Cut Off*
mg/l	*Milligrams per liter*
MSC	*Marcellus Shale Coalition*
NTU	*Nephelometric Turbidity Unit*
PA-DEP	*Pennsylvania Department of Environmental Protection*
PCB	*Polychlorinated Biphenyl Compound*
POGAM	*Pennsylvania Oil & Gas Association*
POTW	*Publicly Owned Treatment Works (Sewage Treatment Facility)*
PPB	*Part per billion (≈µg/l)*
PPM	*Part per million (≈mg/l)*

Q	Flowback recovery rate (bbl-day^{-1})
QAPP	Quality Assurance Project Plan
t	Variable representing time (days)
T	Time (days)
TCEQ	Texas Commission on Environmental Quality
TCF	Trillion Cubic Feet
TDS	Total Dissolved Solids
TPH	Total Petroleum Hydrocarbons
V_A	Total volume of flowback (bbl) at end of flowback period
V_F	Total volume of fracture water used (bbl)
v_R	Variable volume of flowback recovered (bbl) at time t
V_R	Volume of flowback recovered (bbl) at time T
V_U	Total volume of fracture water unrecovered (bbl)
WV-DEP	West Virginia Department of Environmental Protection
WWDB	Texas Water Development Board
µg/l	Micrograms per liter
MVR	mechanical vapor recompression
SCF	cubic foot of natural gas at standard temperature and pressure
TDS	total dissolved solids (mg/l)

1 Introduction

The Barnett and Marcellus Shales are among the largest and most active natural gas plays in the U.S. covering all or part of 20 counties in North Texas and large areas of Pennsylvania, Ohio, New York, and West Virginia. Eagle Ford has become notable as one of the most rapidly expanding development regions, growing in permits from 33 and 94 in 2008 and 2009, respectively, to 1,229 drilling permits in 2010. These natural gas shale basins are shown in Figure 1-1. The Barnett area has approximately 2.5 trillion cf^3 of natural gas reserves and is estimated to contain up to 27 trillion cf^3 of recoverable natural gas (USGS, 2004; Clouser, 2006). The Marcellus Play of the Appalachian Shale Region is larger in comparison to the Barnett. These unconventional plays require pumping of significant volumes of water for hydraulic fracturing to initiate natural gas production.

Figure 1-1: Shale Gas Basins in the U.S.

Hydraulic fracturing (fracking) is a necessary step for economic well performance, requiring between 1 and 5 million gallons of water, sand and chemicals to be injected downhole under high pressure for successful well completion. Vertical wells require approximately 1 million gallons and horizontal wells require 3-5 million gallons according to a recent survey among Barnett Shale Producers. The same per-well water use applies to the Appalachian Shale. Of the total water used by the industry, frac jobs represent about 89% and drilling represents 10%. Water demand poses a number of challenges for industry in developing the Barnett and Appalachian Shales for natural gas production. The industry must procure large volumes of the water, often amid drought conditions. For example, large per-well water amounts multiplied by the 2,000 or more wells completed in the Barnett Region each year requires the industry to find more than 6 billion gallons per year for well completion. In 2005 and 2006, more than half of the water used for well drilling and completion came from groundwater aquifers; the other half came from surface waters.

Because well completion requires very large volumes of water, the pace of development of the Barnett and the Appalachian (Marcellus Play) areas can be potentially constrained by water availability; the same can be stated for other shale gas plays in water-stressed areas. To illustrate, one of the most rapidly growing communities in the U.S. (Dallas-Fort Worth) is situated in the Barnett Shale Region that is naturally limited in precipitation potentially limiting expansion of Barnett Shale development.

Another issue is the cost of managing large volumes of brines that flow back out of the well after completion; this problem is important to most shale gas areas. Water, in fact, is central to many of the environmental impacts of shale gas development. Downhole, flowback water picks up salts, oils, and completion chemicals, rendering the water unsuitable for surface discharge; therefore the water is often disposed of by subsurface injection.

For most shale gas plays, the management of water for fracturing is so large that it comprises a major annual cost in terms of transportation, handling, and environmental control. The movement of a million gallons of water from surface water impoundments to the well pad requires 210 trucks. Delivery of 4 million gallons of water would require over 840 truckloads. Movement of the flowback and produced waters collected after well completion requires 210 truckloads for every million gallons of wastewater transported, if off-site disposal of the collected flowback water is required. Water handling and transportation affect multiple environmental factors including emissions, carbon footprint, traffic congestion, perceived public nuisance, public safety, and frequency of emergency spills and releases.

Predominantly, the industry prefers to dispose of flowback and produced waters using Class II deep well injection if such disposal capacity is locally available and economically accessible. In areas of the U.S. where Class II wells are sparse (the Marcellus Shale has only 7 Class II wells which represents a very low capacity to accept produced waters and flowback), water reuse has been a logical alternative to pursue as is done in the Pennsylvania portion of the Marcellus Shale. In areas of the U.S. where severe limitations of water availability can arise from frequent occurrences of drought, shale gas developers have considered water reuse as a means of significantly reducing demands on sources of fresh water that compete with community water supplies.

Information on water flows in the shale gas industry indicate that although each well completion represents a potential significant flowback water output equivalent to 5-35% of the influent water, it is also true that future hydraulic fractures represent substantial opportunities for the reuse of these waters, especially during the growth phase of each shale gas development area. The median flowback water volume collected from 19 locations in the Marcellus Shale was approximately 24 percent of the influent water volumes used for each completion operation.

In recent years, water reuse (i.e. the strategy of recycling flowback and produced waters collected from a completed well and blending the recovered water with freshwater to supply the influent water for the next hydraulic fracturing event for a future well completion) has been increasingly embraced by the industry for its benefits in water conservation and in significantly reducing transportation. Every barrel that is reused within a well field area is one barrel less of fresh water required for the next frack job. Every barrel that is reused is also one less barrel of water that requires transportation and disposal. Reduced transportation means reduced traffic and road wear, a lower visibility with the public, less air emissions and lower carbon footprint ---- comprising environmental benefits on multiple levels.

Various energy developers are working to define the minimum water quality specifications for the influent water used for effective hydraulic fracturing. The Barnett Shale Water Conservation and Management Committee conducted its own Frack Job Expert Panel to discuss the minimum quality of water required for hydraulic fracturing (Hayes, 2007). Among the top concerns was salinity of the final water blend to be injected during the frac job because high salt concentrations caused existing friction reducers to lose their effectiveness; high salinity made it necessary to add more friction reducers to avoid having to apply excessive downhole pressures for the frack job. A number of developers have examined brine treatment processes to condition waters for reuse. In addition to conventional processing for removing suspended solids, oils and greases, and microbes, energy companies have also evaluated membranes and thermal distillation (i.e. mechanical vapor recompression) for their efficacy in achieving recovery of demineralized water for reuse.

Where flowback and produced water reuse are pursued, there are mainly two schools of thought that exist in the shale gas industry regarding overall approach. Approach “A” is comprised of conditioning the brines for the removal of suspended solids, oils and greases, bacteria, and scale forming ions (i.e. constituents that potentially interfere with equipment and infrastructure maintenance) with no demineralization (desalination) prior to reuse. Currently, this approach is being used within the Marcellus Shale as the predominant shale gas water management practice. A more rigorous treatment (“Approach B”) is comprised of treating shale gas water all the way to the recovery of distilled or demineralized water with the concomitant generation of a small volume of concentrated brine; this rigorous treatment approach is usually capable of recovering demineralized water equivalent to 70-80% of the original flowback/produced water stream.

Against this backdrop, the industry has been active in a cooperative manner in understanding its water management issues and in evaluating effective management solutions. In 2006, the developer companies of the Fort Worth Basin formed the Barnett Shale Water Conservation and Management Committee with a mission to develop best management practices to ensure water is managed in an environmentally responsible manner. In the same spirit, the Appalachian Shale Water Conservation and Management Committee was formed in 2008 to provide the means of developer companies to cooperate together in identifying effective approaches for sustainable water management in the Marcellus Shale Play; this industry group was later integrated into the larger Marcellus Shale Coalition which addresses a more comprehensive scope of challenges related to the shale gas industry. Through involvement with all three organizations, GTI has been able to become a part of an on-going conversation in the industry concerning water management challenges and potential solutions. Informed by industry perspective and priorities of the Barnett and Appalachian Shale Regions, GTI with the input of the BSWCMC and the ASWCMC prepared a proposal to RPSEA with a scope of work that addressed the key issues identified by the industry.

This is the “final” report that describes the GTI research project supported by the RPSEA-NETL program; the project was entitled, “Barnett and Appalachian Shale Water Management and Reuse Technologies”. The overall purpose of the project was to pursue a number of research directions that address the priority challenges of the industry in shale gas water management. The project, which was initiated in August of 2009, has generated thirteen reports that discuss the methods, data and findings in considerable detail. This Final Report presents the most important information and highlights from these reporting deliverables which are available in electronic format from RPSEA upon request.

2 Program Overview

Contract Number	08122-05	Start Date	August, 2009	End Date	March, 2012
Total Months	32	RPSEA Share	$2,500,000	Cost Share	$640,000
Prime Contractor	Gas Technology Institute (GTI)	Subcontractors	Bureau of Economic Geology (BEG), The University of Texas, Texerra, GeoPure Hydro Technologies, Advanced Hydro, Inc., and Environmental Process Dynamics.		

Overall Objective

The overall objective of this proposal is to develop water management methods and technologies that reduce demands for freshwater, reduce environmental impact of brine disposal, and ensure supplies of water for well drilling and completion for natural gas development in the Barnett and Appalachian Shale Plays.

Scope of Work

The project employed a balanced approach aimed at improving technologies for water treatment for demineralization, water reuse, and water conservation. Specific areas of emphasis included: 1) Evaluation of promising commercially-available technologies for water reuse; 2) Development of novel coatings to improve performance and cost of ultrafiltration, nanofiltration and reverse osmosis treatment technologies in the demineralization of flowback waters; 3) Development of electrodialysis reversal for low-cost produced water and flowback water demineralization; and, 4) Identification and evaluation of alternate sources of water that may be useful as replacements for groundwater or surface waters that serve as community water supplies. The tasks of the project are described in Table 2-1.

Table 2-1 Tasks of the GTI Project and Performing Organizations

Task #	Task Description	Performing Organizations
1	Prepare Project Management Plan.	GTI
2	Prepare Technology Status Assessment.	GTI
3	Pursue technology transfer activities.	GTI
4	Develop shale flowback / produced water characteristics information base.	GTI
5	Determine the feasibility of low salt content early flowback water capture.	Texerra
6	Determine the feasibility of locating and developing alternate sources of water in the Barnett for shale gas production that do not compete with community water	Bureau of Economic Geology

Task #	Task Description	Performing Organizations
	supplies.	
7	Conduct engineering evaluation of the field performance and cost of a Mechanical Vapor Recompression distillation unit in the demineralization of flowback and produced waters for shale gas water reuse.	GTI, Environmental Process Dynamics (EPD)
8	Develop electrodialysis for fouling-resistant, demineralization (desalination) of shale gas flowback and produced waters.	GTI, Environmental Process Dynamics (EPD)
9	Develop innovative coatings for the improvement of ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) in the demineralization of shale gas flowback and produced waters.	The University of Texas (UT)
10	Evaluation of field performance of innovative coatings for UF and RO membranes in the treatment of shale gas flowback and produced waters.	UT, GeoPure, Advanced Hydro,
11	Engineering systems analysis of a preliminary water based life cycle model to forecast water issues for development areas and well fields.	GTI, EPD
12	Project coordination with shale gas industry companies and committees and participate in periodic review with industry of the progress of the key activities.	GTI
13	Prepare Final Report.	GTI

Technical tasks in the above table are shown in the shaded areas, Tasks 4-11. The methods and accomplishments of these tasks are described in Chapters 4-11 of this report. The activities and accomplishments that contributed to Tasks 3 and 12 are described in Chapter 12. Tasks 1 and 2 are planning and project scoping tasks that were requested by RPSEA; these tasks were completed and the reports for these tasks were submitted to RPSEA in the first month of the project before work on the other tasks were initiated.

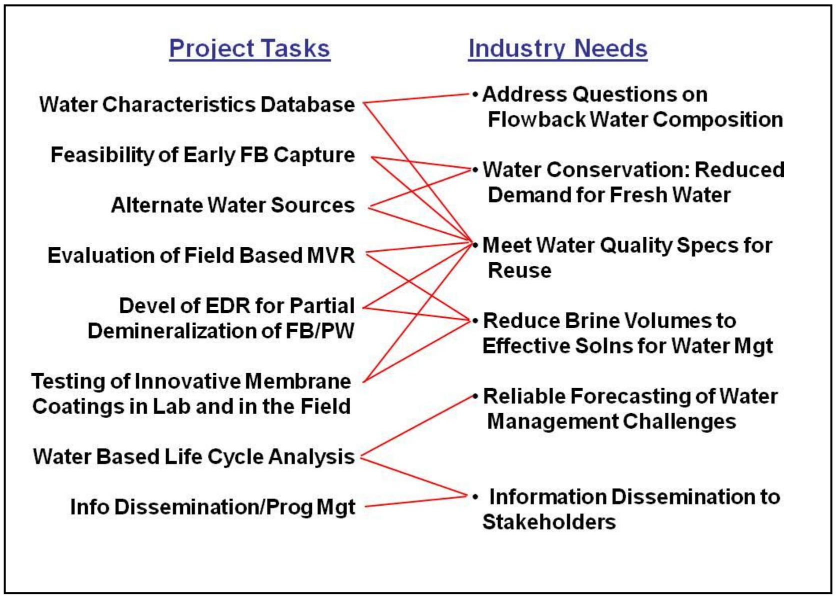

Figure 2-1: Industry Needs Addressed by Project Tasks

The tasks of the project were designed and planned with the input of the shale gas industry through the advice of companies in the BSWCMC. The tasks of Table 2-1 address key industry needs as described in Figure 2-1. As see in the figure, the water issues of the industry are diverse, ranging from conservation to addressing questions on chemical additives and flowback water composition, from meeting water quality specifications for reuse to reducing brine volumes to achieve cost reductions in transportation. Prediction and forecasting of water management issues and the severity and nature of the challenges the problems present is a relatively new industry need that has important implications in business planning, cost control and liability management; this is discussed in greater detail in Chapter 11 which describes the Water Based Life Cycle Model and analysis results.

Reporting Deliverables

Each of the chapters to follow will cite certain topical reports that contain more detailed information and were submitted to RPSEA for distribution. These 14 deliverable reports are described in Table 2-2.

Table 2-2: Deliverable Reports that Are Referenced in the Final Report.

Title	Authors
Development of Electrodialysis for Shale Gas Water Reuse. RPSEA Report No. 08122-05.01. November 2010.	Blaine Severin, Tom Hayes
Membrane Fouling Reduction Test Plan – Processing Shale Gas Flowback and Produced Water. RPSEA Report No. 08122-05.02. December 2010.	Steve Shiner, Robert Hayes Dileep Agnihotri, Richard Li Xiaofei Huang, Peach Sirirat Albert Li
Innovative UF / NF / RO Membrane Performance Through the Use of Innovative Coatings: Selection of Membrane Supports and Coatings for Barnett Well Flowback Water Separations. RPSEA Report No. 08122-05.03. November 2010.	Albert Li, Sirirat Kasemset Daniel J. Miller, Benny D. Freeman, Mukul M. Sharma
Feasibility of Using Alternative Water Sources for Shale Gas Well Completions – A Preliminary Guidance Document on the Current Practices in the Barnett. RPSEA Report No. 08122-05.04. February 2011.	Jean-Philippe Nicot
Field Assessment and Anti-Fouling Polymeric Membrane Coatings for Treatment of Barnett Shale Flowback Produced Water. RPSEA Report No. 08122-05.05. March 2011.	Xiaofei Huang, Dileep Agnihotri Benny D. Freeman, Robert Hayes Sirirat Kasemset, Albert Lee Hua Li, Mukul Sharma, Steve Shiner
Feasibility and Design Approach for Automatic Classification and Segregation of Early Flowback Water for Reuse in Shale Gas Hydraulic Fracturing. RPSEA Report No. 08122-05.06. July 2011.	L. Peter Galusky
Feasibility Assessment of Early Flowback Water Recovery for Reuse in Subsequent Well Completions. RPSEA Report No. 08122-05.07. October 2011.	L. Peter Galusky
Feasibility of Using Alternative Water Sources for Shale Gas Well Completions. RPSEA Report No. 08122-05.08. January 2012.	Jean-Philippe Nicot, Brad D. Wolavar, Yun Huang, Teresa Howard, Ruth A. Costley, Cari Breton, Steven Walden, Russell Baier, and Gil Strassberg
Characterization of Flowback Waters from the Marcellus and the Barnett Shale Regions. RPSEA Report No. 08122-05.09. February 2012.	Thomas D. Hayes, Blaine F. Severin
Preliminary Engineering Systems Analysis of Shale Gas Water Management. RPSEA Report No. 08122-05.10. February 2012.	Thomas D. Hayes, Blaine F. Severin

Title	Authors
Engineering Decision Tool for the Evaluation of Mechanical Vapor Recompression for the Treatment of Shale Gas Flowback Water. RPSEA Report No. 08122-05.11. February 2012.	Thomas D. Hayes Blaine F. Severin
Evaluation of Electrodialysis in the Demineralization of Shale Gas Flowback Waters. RPSEA Report No. 08122-05.12. February 2012.	Blaine F. Severin Thomas D. Hayes
Novel Fouling-Resistant Membranes for Barnett Shale Water Management and Reuse. RPSEA Report No. 08122-05.13. February 2012.	Albert Lee, Sirirat Kasemset Daniel J. Miller, Benny D. Freeman, Mukul M. Sharma
Final Report: Barnett and Appalachian Shale Water Management and Reuse Technologies. RPSEA Report No. 08122-05.14. March 2012	Thomas D. Hayes, Blaine F. Severin

Accomplishments

In general, all goals that were established for the tasks of this project have been achieved. Looking across all activities of the project, the most important accomplishments are as follows:

1. Reduced energy demands for membrane-based demineralization of shale gas waters by more than 35% through the use of innovative coatings on the membrane surfaces of ultrafiltration and reverse osmosis. This was successfully demonstrated in the lab and in the field.
2. Innovative coatings for RO are now commercially available from Advanced Hydro and applied in the shale gas production field by GeoPure.
3. Reduced energy demands for electrodialysis (ED) demineralization of flowback water by more than 40% and chemical inputs by 65% compared to conventional ED processing. Improvements in design have led to three invention disclosures for robust, fouling-resistant, processing of high-hardness flowback and produced waters.
4. Verified the successful operation of a high-efficiency, mechanical vapor recompression (MVR) in the conversion of flowback and produced waters under actual field conditions over a prolonged period.
5. Developed an integrated flowback water characteristics information base for the Barnett and Marcellus shale plays.
6. Completed a GIS framework and protocol for locating and estimating significant alternate water sources of water for shale gas development that do not compete with community water supplies in the Barnett Shale Region.
7. Developed a means of capturing low-salt-concentrated water through an automated water flow segregation method based on in-line conductance measurements and automatic switching of flows into separate basins as flowback water is generated from a frac job.
8. Tech Transfer: Participated in six workshops and numerous technical forums with 13 presentations (see listing).

Significant Findings

- Completed data collection for an 8-week detailed evaluation of a patented mechanical vapor recompression (MVR) process operated by Fountain Quail at a Devon Energy water reuse facility under highly varied influent conditions. Results indicated that the MVR technology was able to process produced water with salt concentrations up to 60,000 mg/l while achieving demineralized water recovery efficiencies exceeding 74% at modest natural gas utilization levels averaging only 48 scf per barrel (42 gal) of brine fed to the process.
- Innovative polydopamine coatings from University of Texas (UT) applied to ultrafiltration (UF) and reverse osmosis (RO) membranes have significantly reduced fouling by more than half, doubled membrane life and have reduced energy requirements for produced water treatment (demineralization) by more than 35%.
- Using the UT coatings incorporated into commercial membrane modules, an Experimental Test Unit operated in the field by GeoPure (assisted by Advanced Hydro and UT) operated for more than 30 days on flowback and produced waters at a Devon water reuse facility. Under field conditions compared to conventional membranes, coated membranes substantially reduced fouling and enhanced salt rejection performance (< 99.9%) throughout the duration of field testing with brines at concentrations of up to 55,000 mg/l of total dissolved solids.
- Low-cost design modifications for electrodialysis (ED) implemented by GTI and Environmental Process Dynamics (EPD) have been successful at reducing energy costs by more than 40% while lowering chemical costs required for cleaning by more than 65%. Several new design features (including an automated clean-in-place mechanism) that have been incorporated into the process have enabled electrodialysis to handle actual shale gas waters (from four locations in the Barnett and Marcellus Regions) of high hardness (elevated calcium, barium and magnesium) for extended periods without fouling.

3 Organization of Report

The content of this report was provided by all of the subcontractor organizations that comprised the GTI Project Team. The Project Team consisted of GTI, the Bureau of Economic Geology (BEG), The University of Texas, Texerra, GeoPure Hydro Technologies, Advanced Hydro, Inc., and Environmental Process Dynamics. Specific chapter contributions to the Final Report were provided by the following authors and Affiliated organizations.

Table 3-1: Authorship of the Technical Chapters of the Final Report

Chapter #	Chapter Description	Authors
4	Characterization of Flowback Water	Thomas D. Hayes[1] and Blaine F. Severin[2]
5	Feasibility of Capture of Low-TDS Early Flowback Waters	L.Peter Galusky[3] Thomas D. Hayes, and Blaine F. Severin

Chapter #	Chapter Description	Authors
6	Alternate Water Sources for the Barnett Shale	Jean-Philippe Nicot[4], Brad D. Wolaver[4], Yun Huang[4], Teresa Howard[5], Ruth A. Costley[4], Cari Breton[3], Steven Walden[6], Russell Baier[6], Gil Strassberg[7], Ed McGlynn[4], Mary Hingst[4], Joy Mercier[4], and Cliff Lam[4]
7	Evaluation of Mechanical Vapor Recompression Under Field Conditions	Thomas D. Hayes and Blaine F. Severin
8	Evaluation of Electrodialysis for Desalination of Flowback Waters	Blaine F. Severin and Thomas D. Hayes
9	Development of Advanced Membrane Coatings	Albert Lee[8], Sirirat Kasemset[8], Daniel J. Miller[8], Dr. Benny D. Freeman[8], and Dr. Mukul M. Sharma[9]
10	Field Evaluation of Advanced Membrane Coatings	Daniel J. Miller, Sirirat Kasemset, Albert Lee[8], Mukul Sharma, Benny Freeman, Xiaofei Huang[10], Hua Li[10] , Dileep Agnihotri[10] Steve Shiner[11] and Robert Hayes[11]
11	Systems Engineering and Water Based Life Cycle Analysis	Thomas D. Hayes and Blaine F. Severin

Affiliations

1: Gas Technology Institute, Des Plaines, IL
2: Environmental Process Dynamics, Inc., Okemos, MI
3: Texerra, Monument, CO
4: Jackson School of Geosciences, The University of Texas at Austin, TX
5: Center for Space Research, The University of Texas at Austin, TX
6: Steve Walden Consulting, Austin, TX
7: Gil Strassberg Consultant, Austin, TX
8: Department of Chemical Engineering, The University of Texas at Austin, TX
9: Department of Petroleum & Geosystems Engineering, The University of Texas, Austin, TX
10: Advanced Hydro Inc., Austin, TX
11: GeoPure Hydro Technologies, Fort Worth, TX

Each of the above chapters contains concise descriptions of the rationale, approach, goals, achievements, deliverables, benefits and implications of each technical effort, as per the standard final report format requested by RPSEA. Each chapter corresponds to an individual task that was conducted within the GTI project. The details of each effort are provided by topical reports that were prepared and submitted during the performance of the project. The topical reports (thirteen total) are available upon request from RPSEA as they are approved for release to the public in 2012. The summary final report plus 13 topical reports allow a large amount of information, organized along tasks, to be electronically disseminated as pdf documents in file sizes (< 10 megs) that are easily downloaded from the RPSEA website or sent by email.

4 Characterization of Flowback Waters from the Marcellus and the Barnett (Task 4)

Rationale

This report addresses water management needs by elucidating the chemical nature of flowback waters from 19 sites in the Marcellus region of Pennsylvania and West Virginia and 5 sites from the Barnett region of northern Texas. The database includes flowback rates, volumes, and chemical analyses of the injected water and the recovered flowback water. Chemical analyses include general chemical information typically used for drinking water analyses. Additionally, the waters were tested for 70 volatile organics, 116 semi-volatile organics, 22 pesticides, PCB's, and 27 metals. The list of chemicals evaluated for this project was co-developed by industrial partners, and state environmental agency representatives.

Objectives

The objective of Task 4 was to present a broad spectrum analysis of the water chemistry in flowback waters from two distinct geographical regions. It is hoped that these data will guide future development of reuse plans, treatment options, and water testing criteria being developed by industry and agencies.

Goals

A major aim of the characterization study was to generate technically sound data.
The field sampling and analysis plan and the quality assurance project plan together comprise the Sampling and Analysis Plan (SAP) (Hayes and Severin, 2012). The SAP was designed to meet the following informational goals:

- Identify specific constituents of interest (COI) associated with flowback water;
- Determine whether hydraulic fracturing additives are a source of COI in the management of water associated with shale gas development; and,
- Provide sufficient information for the selection of proper water management and disposal techniques.

Approach

Seventeen member companies of the Marcellus Shale Coalition volunteered 19 locations for the sampling of influent and effluent water streams. Two companies provided access to five sites in the Barnett. At each location, a well completion was conducted using hydraulic fracturing procedures that involved the injection of an influent stream of water and the subsequent collection of a flowback water. Standard procedures were used to conduct sampling and analysis needed for the development of water characterization data. All sampling was performed by the GTI subcontractor, URS, following the same standard procedures. All sample analyses were performed by a single laboratory, Test America of Pittsburgh, PA.

Prior to initiating the characterization study, the SAP was reviewed by regulatory officials from the Pennsylvania Department of Environmental Protection (PADEP) and the West Virginia Department of Environmental Protection (WVDEP).

The original SAP proposed that four (4) grab samples from six (6) vertical or horizontal well locations throughout West Virginia and Pennsylvania. The following grab samples were proposed:

- One baseline fracturing water sample that includes the fracturing chemicals, excluding the sand;
- Flowback water samples will be collected on days 1, 5 and 14 of the following the fracturing process (Marcellus samples) days 1, 3, 5 and 10 for sites in the Barnett.
- Water from an existing producing well at 90 days (Marcellus) and day 10 (Barnett) following hydraulic fracturing.

The list of constituents recommended for the characterization study was developed from comments received from the PADEP, the WVDEP and members of the Appalachian Shale Water Conservation and Management Committee (ASWCMC). Because the recommended list of constituents was extremely extensive, it was decided that one sample from each site would be completed for the full list of recommended constituents. All other samples were collected and analyzed for a subset of these constituents, which was designed based on generator knowledge. A complete list of all the chemicals sought for in the analyses is presented in the full topical report for Task 4 (Hayes and Severin - RPSEA Report No. 08122-05.09, 2012).

Results from the Marcellus

The flow volumes and total salt concentration profiles for the Marcellus data base have been reviewed extensively elsewhere (see Hayes and Severin - RPSEA 08122-05.09, 2012) and are not reproduced, herein, for brevity.

General Chemistry: A summary of the general chemical characteristics of the water influent streams (raw water) and the fracture water associated with the initiation of the fracing process are presented in Table 4-1. Raw Source water is compared against blended water containing conditioning chemicals (minus sand). Dissolved solids measurements for the influent waters used for hydraulic fracturing (with additives) had a median value of 735 mg/l, which is considered in the range of fresh surface water supplies. Oil and grease measurements had a median value of almost 30 mg/l with a range of 0.5 to 255 mg/l. Total organic carbon had a range of 5.6 to 1,260 mg/l with a median of 226 mg/l; elevated values in these measurements may be due to various degrees of blending of reused waters into frac job influent water supplies. Additives blended into the raw water, or reused water blended into the supply resulted in slight increases in some water quality parameters such as BOD, COD, total Kjeldahl nitrogen and ammonia.

Table 4-1: Summary of Chemical Characteristics of Water Used for Hydraulic Fracture Marcellus Samples

Parameter	Raw Source[1] Water		Blended[3,4] Frac Water		Units
	Range	Median	Range	Median	
pH	6.7-7.3	7.1	6.0 - 8.9	7.2	No Units
Acidity	< 5 – 5.5	< 5	< 5 - 1230	< 5	mg/l
Total Alkalinity	6.2 – 88.8	71.4	< 1 – 308	81.8	mg/l
Hardness as CaCO3	18 - 1,080	140	26 - 9,500	130.0	mg/l
Total Suspended Solids	<2 – 24	9.6	< 2 - 5,290	155.0	mg/l
Turbidity	1.3 – 33.7	4.3	2.7 – 715	249.0	NTU
Chloride	4.1 – 3,000	42.3	18 - 10,700	90.2	mg/l
Total Dissolved Solids[2]	51 – 5,510	390	221 - 27,800	735.0	mg/l
Specific Conductance	54.8 – 10,100	466	177 - 34,600	726.0	umhos/cm
Total Kjeldahl Nitrogen	< 2.3 – 56.4	2.2	2.3 – 400	33.5	mg/l
Ammonia Nitrogen	< 0.24 – 20.8	0.52	0.58 – 441	5.9	mg/l
Nitrate-Nitrite	< 0.01 – 3.0	0.51	< 0.032 - 0.34	0.1	mg/l
Nitrite as N	< 0.0032 – 4.9	< 0.0032	< 2.0 – 1740	271.0	mg/l
Biochemical Oxygen Demand	< 2.0 – 110	< 2.0	< 4.3 - 47,400	1730.0	mg/l
Chemical Oxygen Demand	< 4.3 – 924	18.4	5.6 - 1,260	226.0	mg/l
Total Organic Carbon (TOC)	1.8 – 202	3.8	5 - 1,270	301.0	mg/l
Dissolved Organic Carbon	1.4 – 222	3.2	< 0.49 – 255	29.2	mg/l
Oil & Grease (HEM)	-	< 0.5	< 1.7 – 680	4.6	mg/l
Cyanide, Total	< 1.7 – 625	< 1.7	< 0.005 - 0.87	< 0.005	µg/l
Amenable Cyanide	< 0.005 - 0.3	< 0.005	< 0.014 – 107	0.9	mg/l
Bromide	< 0.0014 – 1.9	0.14	< 0.004 - 58.3	0.004	mg/l
Fluoride	< 0.004 - 1.2	< 0.004	< 1.2 - 8.8	< 1.2	mg/l
Total Sulfide	1.2 - 5.6	1.6	< 0.031 – 2920	50.3	mg/l
Sulfate	3.8 – 139	43.7	< 0.03 – 16	0.14	mg/l
Total Phosphorus	< 0.03 – 0.1	0.044	< 0.0057 - 0.77	0.033	mg/l
Total Recoverable Phenolics	0.0057 - 0.14	0.0065	0.05 – 0.50	0.05	mg/l
Methylene Blue Active Substances (MBAS)[3]	0.05 – 0.50	0.05	6.0 - 8.9	7.2	mg/l

[1] Water Supplies at 7 Locations: F, H, I, J, L, M, S. [2] Upper end concentrations in the TDS range may be due to implementation of flowback water reuse and blending into the influent stream. [3] Data analysis for 8 Locations: D, F, H, I, J, M, N, S. [4] Additives included corrosion inhibitors, scale inhibitors, friction reducers, biocides, and oxygen scavengers. Blended water samples were taken before the addition of sand.

Results from Day 1 and Day 14 are presented in Table 4-2. Day 1 results, in general, show a huge range of values, indicating the rapid change in concentrations with initiation of flowback. By Day 5, most sites are demonstrating concentrations trending toward the maximum seen by Day 14 or Day 90. Day 14 results, in general, show a large range of values, based on one sample from Site K that was generally less concentrated than the 5 Day sample. Day 5 and Day 90 data may be found in the full report (See Hayes and Severin – RPSEA Report No. 08122-05.09, 2012).

All water samples show relatively modest alkalinity with median values of 85–120 mg/l, reflecting low carbonate concentrations which allows for very high concentrations of soluble calcium. This confers a very high hardness on the water as evidenced by median hardness values of 17,700 and 34,000 mg/l for the 5-day and 14-day sample sets, respectively. Cations are dominated by sodium and calcium in this water; anions are dominated by chloride.

Table 4-2: Range of Results from 1 and 14 Day Samples

General Chemistry	Day 1		Day 14 (17 Sites Reporting)		
	Range	Median	Range	Median	Units
pH	5.9 - 7.9	7.4	4.9 - 6.8	6.2	No Units
Acidity	ND		19.4 - 473	114	mg/l
Total Alkalinity	107 - 577	251	26.1 - 121	85.2	mg/l
Hardness as CaCO3	156 - 25,000	4,150	630 - 95,000	34,000	mg/l
Total Suspended Solids	6.8 - 522	71	17 - 1150	209	mg/l
Turbidity	10 - 461	52.1	10.5 - 1090	233	NTU
Chloride	64.2 - 151,000	9,890	1,670 - 181,000	78,100	mg/l
Total Dissolved Solids	680 - 122,000	18,900	3,010 - 261,000	120,000	mg/l
Specific Conductance	479 - 645,000	37,750	6,800 - 570,000	256,000	umhos/cm
Total Kjeldahl Nitrogen	14.2 - 158	52.9	5.6 - 261	116	mg/l
Ammonia Nitrogen	2.8 - 173	32	3.7 - 359	121	mg/l
Nitrate-Nitrite	0.01 - 2.8	0.5	0.025 - 0.92	0.25	mg/l
Nitrite as N	ND - 6.7	3.1	1.7 - 77.4	18.75	mg/l
Biochemical Oxygen Demand	27.6 - 1,440	327.5	2.8 - 2070	39.8	mg/l
Chemical Oxygen Demand	397 - 10,700	1,660	228 - 21,900	8530	mg/l
Total Organic Carbon	2.2 - 672	142	1.2 - 509	38.7	mg/l
Dissolved Organic Carbon	20.2 - 657	253	5 - 695	43	mg/l
Oil & Grease (HEM)	5.7 - 53.9	13.7	7.4 - 103	30.8	mg/l
Cyanide, Total	6.6 - 177	21.5	1.9 - 7.4	5	ug/L
Bromide	35.5 - 376	120	15.8 - 1,600	704	mg/l
Fluoride	0.077 - 32.9	0.975	ND - 2	-	mg/l
Total Sulfide	1.6 - 3.2	1.6	1.6 - 3.2	2	mg/l
Sulfate	10.7 - 348	46	0.078 - 89.3	40	mg/l
Total Phosphorus	0.037 - 21.8	0.18	0.035 - 2.2	0.115	mg/l
Total Recoverable	0.007 - 0.064	0.027	0.006 - 0.31	0.016	mg/l

Levels of total organic carbon (TOC) in the flowback water samples at 5 and 14 days (with median values of 63 and 39 mg/l) are substantially lower (by about 75%) than the TOC of the blended influent water with additives; a possible reason for this is that the polyacrylamide friction reducers exert a TOC in the influent stream and are removed as water resides in the down-hole environment. The same observation is made in comparing biochemical oxygen demand (BOD) values in flowback water with the BOD of the influent water streams; in general, the BOD levels of the 5-day and 14-day flowback waters are less than half the influent BOD concentrations. The moderate levels of BOD in the influent waters may have resulted from carbonaceous algae growth in the source water or resulted from the biodegradable nature of the additives (e.g. polyacrylamide friction reducing compounds). The loss of friction reducing compounds due to adherence to surfaces downhole may be responsible for the lower BOD concentrations in flowback waters.

***Volatile Organic Chemicals (VOC)*:** Samples collected from Locations A through S were analyzed for 70 volatile compounds of highly varied chemical characteristics, including the volatile hydrocarbon constituents that are normally found in produced water (such as benzene, toluene, ethylbenzene, and xylenes – or BTEX, and naphthalene) as well as constituents not known to be associated with conventional produced water such as chlorinated solvents and halogenated aromatics.

Source water (fracture water) data (Day 0 minus sand) are presented in Table 4-3. Of 1330 measurements, only 92 observations of volatile compounds were made. Acetone was measured in 12 samples, representing the use of acetone as a component of the additives. BTEX and alkylated benzene isomers likely represent a component of water reuse from previous sites. Traces of halogenated solvents occasionally occur at the part per billion level. Apparently, the additives used in the fracking process do not manifest themselves amongst the most problematic volatile components.

Table 4-3: Influent Water (Fracture Water) Day 0 (minus sand) from Marcellus Database

Volatiles	Observations	Range µg/l		Median µg/l
Naphthalene	7	0.55-	820	3.8
n - Propylbenzene	1	ND-	2	
1, 2, 4 - Trimethylbenzene	10	0.72-	140	9.15
1, 3, 5 - Trimethylbenzene	7	2.8-	100	7.7
Isopropylbenzene	2	0.95-	0.95	0.95
2 - Butanone	2	3.6-	7.5	5.55
Xylenes (total)	11	2.6-	210	18
sec - Butylbenzene	2	3.2-	84	43.6
Acetone	12	5.4-	170	17.5
Benzene	4	2.2-	6.7	6.7
Bromodichloromethane	1	ND-	2	
Bromoform	4	7.8-	9.3	8.55
Carbon disulfide	4	1.6-	54,000	12,250
Chloroform	1	ND-	2.4	
Dibromochloromethane	1	ND-	2.1	
1, 2 - Dichloroethane	1	ND	2.6	
Ethylbenzene	5	0.81-	19	1.7
Methylene chloride	1	ND-	13	
Tetrachloroethene	2	1.3-	1.4	
Toluene	13	0.93-	81	5.6
Trichloroethene	1	ND-	0.81	
Total Observations	92	of	1330	measurements

The organic components, unlike total salts, do not follow a timed based profile. In general, their appearance in the flowback waters appears anywhere from low and constant or intermittent and random. As such, the best means of presenting the volatile data for the 19 sites is to present tablulated distributions, ie., the number of observations within a stated concentration range. Table 4-4 shows the distribution of observations for all 60 samples. As an example, p-Isopropyltoluene was observed once at a concentration between 50–99 µg/l, twice between 10–49 µg/l, once between 1-4.9 µg/l, and undetected (ND) in 56 samples. Many of the compounds were observed only once in sixty samples, making them either incidental or mistaken. No compound was encountered in all sixty samples. The chemical most likely to be observed was acetone in 48 of sixty samples. Thirty-five of the compounds from the volatiles list were never observed. In total, 4200 measurements were taken and 3710 of them were "non-detects."

Table 4-4: Number of Observations of 70 Volatile Compounds in All 60 Marcellus Samples (Days 1-90)

Number of Observations Between Limits, ug/l	>1000	500-999	100-499	50-99	10-49	5-9.9	1-4.9	ND-1	ND
p - Isopropyltoluene	0	0	0	1	2	0	1	0	56
Naphthalene	0	2	1	0	2	0	8	3	44
n - Propylbenzene	0	0	0	1	0	0	1	0	58
1, 2, 3 - Trichlorobenzene	0	0	0	0	1	1	0	0	58
1, 2, 4 - Trichlorobenzene	0	0	0	0	0	0	1	0	59
1, 2, 4 - Trimethylbenzene	0	4	1	5	8	2	14	5	21
1, 3, 5 - Trimethylbenzene	0	3	2	1	7	6	7	2	32
Isopropylbenzene	0	0	2	1	0	0	2	2	53
2 - Butanone	0	0	0	0	2	2	1	0	55
Xylenes (total)	4	1	8	0	8	7	7	0	25
n - Butylbenzene	0	0	0	0	0	0	1	0	59
sec - Butylbenzene	0	0	0	2	0	0	0	0	58
Acetone	4	1	9	2	26	5	0	0	12
Acrylonitrile	0	0	0	0	0	1	0	0	59
Benzene	3	1	7	1	2	7	7	1	31
Bromoform	0	0	0	0	0	1	0	0	59
Bromomethane	0	0	1	0	0	0	0	0	59
Carbon disulfide	2	0	2	0	1	0	0	0	55
Chloroform	0	0	0	0	1	0	1	0	58
Chloromethane	0	0	1	0	0	1	1	0	57
Ethylbenzene	0	1	4	1	6	1	5	3	39
Methylene chloride	0	0	0	0	0	1	2	0	57
4 - Methyl - 2 - pentanone (MIBK)	0	0	0	0	0	0	0	1	59
Styrene	0	0	0	0	0	0	1	0	59
Tetrachloroethene	0	0	0	0	0	1	0	0	59
Toluene	5	4	4	2	3	2	19	2	19
All 35 Others	0	0	0	0	0	0	0	0	2450
Total	18	17	42	17	69	38	79	19	3710

Constituents that exceeded 100 ppb included components that are commonly present in conventional produced water, such as naphthalene, BTEX, several methylated benzene compounds and an alkylated toluene (p-isopropyltoluene). Few determinations of these compounds exceeded 1 ppm and only one occurrence was above 2 ppm. In the locations where BTEX was measured at levels above 100 ppb, BTEX levels in the 5-day and 14-day flowback waters that were in contact with the natural gas producing formation were generally higher than BTEX concentrations in the influent water streams, indicating that these compounds are naturally occurring and not the result of additives. Levels of BTEX and methylated aromatics vary from location to location. Determination of factors that control levels of these compounds could potentially be determined through a correlation of the composition of volatiles and other flowback water characteristics with the key shale gas development parameters of geographic area, depth of wells, completion methods, etc.

In total, 4200 chemical tests for VOC's were performed in the 60 sample data set. Of these observations, 3710 were below detection limits and 472 were below 1 ppm (µg/l). Those samples (18 total) above 1 ppm included acetone, xylenes, carbon disulfide, and toluene. Figure 4-1 is a distribution plot showing these basic trends.

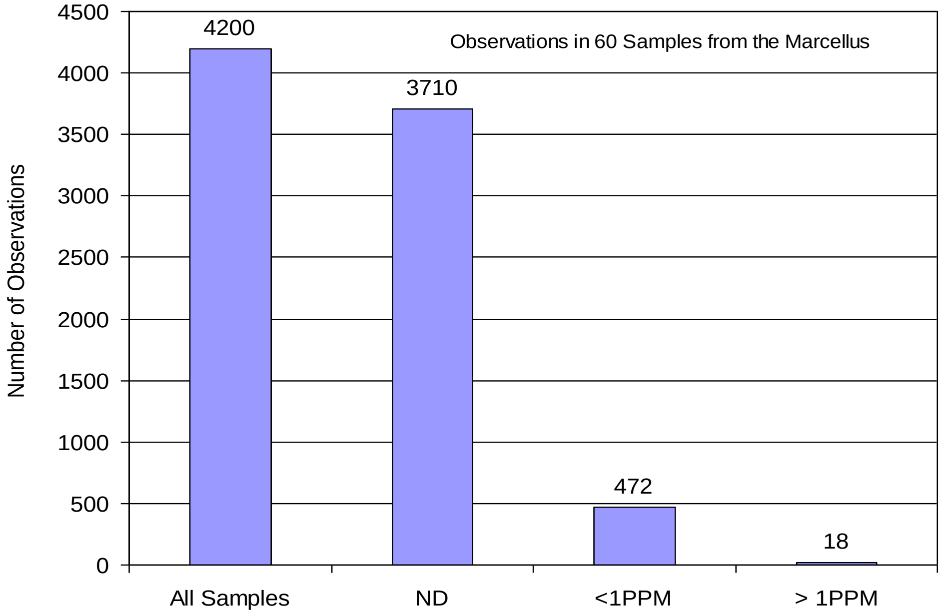

Figure 4-1: Distribution of Observations for 70 Volatile Organics in 60 Samples from the Marcellus

Semivolatile Compounds: A total of 112 semivolatile organic compounds were included in the analysis of influent water and in flowback water samples. A summary of the results for the semivolatile determinations on hydraulic fracturing influent water samples (consisting of the influent water plus chemical additives minus sand) is presented in Table 4-5. The most commonly-encountered semivolatiles belong to the phthalate ester group, probably representing trace compounds introduced as plasticizers. Pyridine is commonly encountered and possibly represents a trace residue from the manufacture of some of the polymeric additives (such as friction reducers).

Table 4-5: Semi-Volatile Content in 19 Marcellus Influent Samples (Fracture Water)

Source Water Day 0	Observations In 19 Samples	Range, µg/l	Median of Observations, µg/l
Acetophenone	1	ND - 0.97	0.97
Benzo (a) anthracene	1	ND - 1.1	1.1
Benzo (a) pyrene	1	ND - 6.9	6.9
Benzo (b) fluoranthene	1	ND - 11	11
Benzo (ghi) perylene	1	ND - 7.4	7.4
Benzo (k) fluoranthene	1	ND - 6.7	6.7
Benzyl alcohol	2	74 - 74	74
bis (2 - Chloroethyl) - ether	1	ND - 4300	4300
bis (2 - Ethylhexyl) phthalate	11	2 - 21	9.4
Butyl benzyl phthalate	1	ND - 5.1	5.1
Chrysene	1	1.7 - 1.7	1.7
Dibenz (a, h) anthracene	1	ND - 12	12
Di - n butyl phthalate	9	0.29 - 1.7	0.6
1, 2 - Dichlorobenzene	1	ND - 0.68	0.68
1, 4 - Dichlorobenzene	1	ND - 0.6	0.6
2, 6 - Dichlorophenol	1	ND - 2	2
Diethyl phthalate	2	0.49 - 1.8	1.145
2, 4 - Dimethylphenol	1	ND - 0.39	0.39
Fluoranthene	1	ND - 5.5	5.5
Fluorene	2	0.83 - 1.2	1.015
Indeno (1, 2, 3 - cd) pyrene	2	10 - 10	10
2 - Methylnaphthalene	7	1.3 - 300	7.5
Naphthalene	6	0.61 - 1800	4.3
Phenanthrene	7	0.28 - 24	1.3
2 - Picoline	1	ND - 5.3	5.3
Pyrene	3	0.19 - 0.54	0.22
Pyridine	9	0.91 - 510	17
All 89 Other Chemicals	0	ND	ND

For all flowback waters (days 1-90), semi-volatile compound determinations that were detectable are listed in Table 4-6. As seen in this table, only four semivolatile constituents were measured in any of the samples at levels exceeding 10 ppb. Acetophenone and aniline are commonly associated with fossil fuels, as are the methylated phenols. The only compound that was measured above 1 ppm was pyridine. Pyridine is a nucleophile used widely in the manufacture of certain chemicals and pharmaceuticals. Its presence may be due to its use as a precursor in the manufacture of one of the hydraulic fracturing additives. Most of the semivolatile determinations were either non-detect (> 96% of the measurements) or at low trace levels (Figure 4-2).

Table 4-6: Number of Observations of 116 Semi-volatile Compounds in All 60 Marcellus Samples

Number of Observations Between Limits ug/l	>1000	500-999	100-499	50-99	10-49	5-9.9	1-4.9	ND-0.99	ND
Diphenylamine	0	0	0	0	0	0	2	0	58
1, 4 - Dioxane	1	0	0	0	15	9	4	2	29
Acenaphthene	0	0	0	0	0	0	0	3	57
Acenaphthylene	0	0	0	0	0	0	0	1	59
Acetophenone	0	0	0	0	6	3	6	9	36
Aniline	0	0	0	0	0	0	2	0	58
Benzo (a) anthracene	0	0	0	0	0	0	2	0	58
Benzo (a) pyrene	0	0	0	0	0	0	2	0	58
Benzo (b) fluoranthene	0	0	0	0	0	0	2	0	58
Benzo (ghi) perylene	0	0	0	0	0	0	3	0	57
Benzo (k) fluoranthene	0	0	0	0	0	0	1	1	58
Benzyl alcohol	0	0	1	0	2	3	1	0	53
bis (2 - Chloroethyl) - ether	0	0	0	0	1	0	0	0	59
bis (2 - Ethylhexyl) phthalate	0	2	0	0	8	9	15	1	25
Butyl benzyl phthalate	0	0	0	0	1	3	0	0	56
Chrysene	0	0	0	0	0	0	2	0	58
Dibenz (a, h) anthracene	0	0	0	0	0	0	2	0	58
Di - n butyl phthalate	0	0	1	1	3	2	5	10	38
1, 2 - Dichlorobenzene	0	0	0	0	0	0	0	2	58
1, 3 - Dichlorobenzene	0	0	0	0	0	0	0	1	59
1, 4 - Dichlorobenzene	0	0	0	0	0	0	0	2	58
Diethyl phthalate	0	0	0	0	1	0	8	4	47
2, 4 - Dimethylphenol	0	0	0	0	3	4	1	2	50
Dimethyl phthalate	0	0	0	0	0	1	0	0	59
Di - n - octyl phthalate	0	0	0	0	2	3	3	0	52
Disulfoton	0	0	0	0	0	0	1	0	59
Ethyl methanesulfonate	0	0	0	0	0	0	0	0	60
Fluoranthene	0	0	0	0	0	5	2	0	53
Fluorene	0	0	0	0	0	2	2	8	48
Hexachlorobenzene	0	0	0	0	0	0	1	1	58
Indeno (1, 2, 3 - cd) pyrene	0	0	0	0	0	0	2	0	58
2 - Methylnaphthalene	0	0	3	2	0	0	9	6	40
2 - Methylphenol	0	0	0	0	3	6	2	3	46
3 - Methylphenol & 4 - Methylphenol	0	0	0	0	7	3	3	13	34
Naphthalene	1	1	0	0	3	1	5	5	44
4 - Nitroaniline	0	0	0	0	0	0	1	0	59
N - Nitrosodiphenylamine	0	0	0	0	0	0	1	0	59
Phenanthrene	0	0	0	0	2	0	5	7	46
Phenol	0	0	0	0	5	0	4	2	49
2 - Picoline	0	0	0	0	1	0	1	0	58
Pyrene	0	0	0	0	1	0	3	5	51
Pyridine	2	2	21	4	5	3	6	0	17
1, 2, 4 - Trichlorobenzene	0	0	0	0	0	0	0	2	58
All 74 Others	0	0	0	0	0	0	0	0	4440
Total	4	5	26	7	69	57	109	90	6593

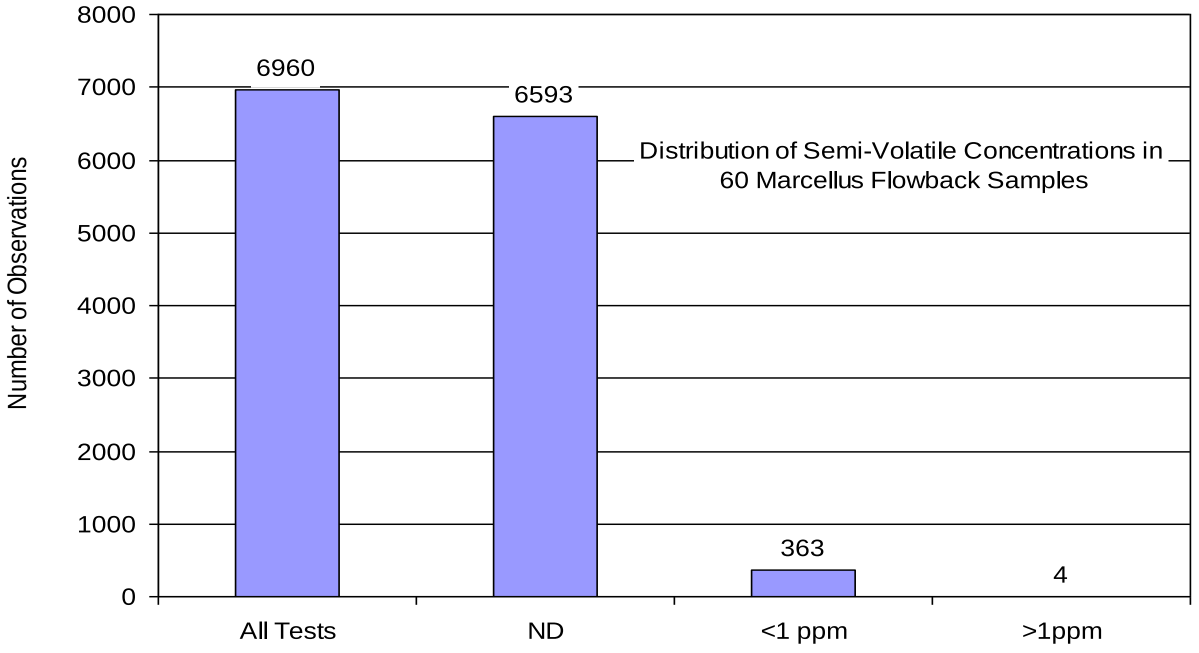

Figure 4-2: Distribution of Observations of Semi-Volatiles in all 60 Marcellus Flowback Samples from 19 Sites

Pesticides: Determinations of the 20 chlorinated pesticides and three organophosphorus pesticides were conducted on the influent and 14-day flowback water streams (Hayes and Severin, RPSEA Report No. 08122-05.09, 2012). None of these pesticides were detected. This would suggest that no chlorinated pesticides were introduced with the additives with the influent water during well completions.

Polychlorinated Biphenyls (PCBs) : Determinations of the 7 polychlorinated biphenyl compounds were conducted on the influent and 14-day flowback water streams; the specific arochlors measured in samples are listed in a previous topical report to RPSEA (Hayes and Severin, RPSEA Report No. 08122-05.09). All determinations for PCBs were measured as non-detect. This would suggest that no PCBs were introduced with the additives with the influent water during well completions.

Metals: Total metals data for the six raw water samples and the 19 influent water samples with additives are presented in Table 4-7. For the most part, the differences in the ranges of concentration between the two sample sets can be explained by the differences expected for the different population (6 vs 19 samples). There is an added unknown statistical bias in the subset of the number of samples in the influent utilizing blended (reused) water versus the number of raw water sources utilizing fresh water.

Table 4-7: Metals Data in Raw Water and Source Water with Additives

Concentrations in µg/l	Raw Water day 0 6 Samples			Influent with Additives 19 Samples		
	Obs	Range	Median	Obs	Range	Median
Aluminum	4	0.122 - 0.264	0.213	5	0.177 - 2	0.4
Antimony	2	0.0146 - 0.0154	0.015	1	0.015 - 0.0154	0.0154
Arsenic	0			0		
Barium	6	0.243 - 5.48	0.589	6	0.108 - 87.1	1.005
Beryllium	0			0		
Boron	5	0.0189 - 2.45	0.0343	5	0.019 - 2.58	0.0433
Calcium	6	4.88 - 40.1	31.75	6	6.69 - 241	32.2
Cadmium	1	0.0017 - 0.0017	0.0017	1	0.002 - 0.0017	0.0017
Cobalt	0	ND		0	ND	
Chromium	0	ND		0	ND	
Chrome III	0	ND		0	ND	
Copper	0	ND		1	0.045 - 0.0445	0.0445
Iron	6	0.192 - 4.31	0.4995	6	0.137 - 3.56	0.4455
Lead	0	ND		0	ND	
Lithium	3	0.0338 - 2.24	0.0422	3	0.03 - 2.34	2.05
Magnesiium	6	1.08 - 183	5.845	6	1.25 - 183	13.87
Manganese	6	0.0087 - 0.237	0.0817	5	0.008 - 0.395	0.127
Molybdenum	0	ND		0	ND	
Nickel	1	ND 0.0111	0.0111	1	0.02 - 0.0195	0.0195
Potassium	4	2.36 - 53.6	2.89	4	2.25 - 57.4	7.265
Sodium	6	4.2 - 1380	31.05	6	32.6 - 1460	59.5
Selenium	0	ND		1	0.035 - 0.0353	0.0353
Tin	0	ND		0	ND	
Strontium	6	0.352 - 76.2	0.6785	6	0.206 - 78.5	0.919
Titanium	1	ND 0.0299	0.0299	2	0.019 - 0.0271	0.0233
Thallium	0	ND		0	ND	
Zinc	6	0.0257 - 0.172	0.0486	6	0.035 - 0.176	0.0635
Mercury	3	5E-05 - 0.00061	5E-05	3	4E-05 - 6E-05	5E-05

Metals data, especially the top five cations, sodum, barium, iron, strontium and magnesium, tend to follow a timed profile. These data are presented by collection day to better show the trends. Summary data for days 1 and 14 are presented in Table 4-8. The 90-day data present a much smaller database (5 sites compared to 17-19 samples in the other sets). The top six metal ions in flowback water are sodium, calcium, magnesium, strontium and iron and potassium. These ions, and most others listed, increase from day 1 to day 90 and represent a significant increase over the raw water and influent water data in the Table 4-8.

Table 4-8: Metals Data for Marcellus Flowback Days 1 and 14

	Day 1 (19 Samples)			Day 14 (17 Samples)		
Metals (mg/l)	Obs	Range	Median	Obs	Range	Median
Aluminum	17	0.165 - 4.03	0.507	5	0.173 - 1.04	0.37
Antimony	13	0.0089 - 0.0378	0.0247	0		
Arsenic	12	0.0133 - 0.0551	0.0333	4	0.0462 - 0.114	0.0726
Barium	19	0.332 - 1450	37.6	5	133 - 4220	1440
Beryllium	0			0		
Boron	19	0.0181 - 13.1	6.68	5	13 - 145	25.3
Calcium	19	35.2 - 19700	833	5	8500 - 24000	18300
Cadmium	4	0.0002 - 0.0029	0.00235	4	0.0025 - 0.0077	0.00255
Cobalt	3	0.0045 - 0.0105	0.0057	0		
Chromium	16	0.0075 - 0.359	0.0318	3	0.0135 - 0.021	0.0177
Trivalent Chromium	6	0.0075 - 0.0491	0.0293	1	ND - 0.0175	0.0175
Copper	11	0.0096 - 0.255	0.0571	2	0.0272 - 0.0515	0.03935
Iron	19	2.68 - 67.2	13.9	5	69.7 - 158	93
Lead	12	0.0017 - 0.0709	0.02565	3	0.0456 - 0.97	0.068
Lithium	18	4.06 - 129	14.05	5	44.5 - 137	88.6
Magnesiium	19	16 - 1320	89	5	933 - 1790	1710
Manganese	19	0.146 - 5.96	0.782	5	2.13 - 9.77	4.72
Molybdenum	19	0.0089 - 0.372	0.0356	1	0.017 - 0.017	0.017
Nickel	17	0.0106 - 0.203	0.0286	0		
Potassium	19	2.69 - 923	109	5	191 - 3950	548
Sodium	19	63.8 - 34700	6290	5	26900 - 75800	39700
Selenium	1	ND - 0.0043	0.0043	1	ND - 0.044	
Tin	3	0.0038 - 0.007	0.0051	0		
Strontium	19	0.58 - 4330	167	5	1220 - 8020	3480
Titanium	11	0.0151 - 0.092	0.0385	4	0.13 - 0.242	0.173
Thallium	3	0.0049 - 0.0272	0.0054	1	0.168 - 0.168	0.168
Zinc	18	0.0561 - 0.665	0.191	5	0.0293 - 0.811	0.178
Mercury	6	4E-05 - 0.000074	5.05E-05	1	ND - 0.000068	

Results from the Barnett

Five sites were sampled in the Barnett. Flowback water samples were collected at the time intervals indicated in Table 4-9. Initial raw water for Sites LPG1 and LPG2 was from the same source and is represented by a single sample. Initial raw water for Sites LPG 3, LPG 4, and LPGX was from the same source and is represented as a single sample. Four of five sites reported on Day 1. Three sites reported on Day 5 and one site reported on Day 6. These four samples dates are treated together in discussions of Day 5-6 events. Three sites reported on Day 10 and one site reported on Day 12. These sample dates are treated together in discussions of Day 10-12 events. The flow volumes and total salt concentration profiles for the Marcellus data base have been reviewed extensively elsewhere (See Hayes and Severin – RPSEA Report No. 08122-05.09, 2012) and are not reproduced, herein, for brevity.

Table 4-9: Sample Dates (Days after Fracture) for 5 Sites in the Barnett

	Day 0	Day1	Day 3	Day 5	Day 6	Day 7	Day 10	Day 12
LPG1	🟧	X	X	X			X	
LPG2	🟧	X	X	X			X	
LPG3	🟩	X		X		X		X
LPG4	🟩		X		X		X	
LPG X	🟩	X						

General Chemistry: A summary of the general chemical characteristics of the two water influent samples presented in Table 4-10. The pH of these streams ranging from 7.7 to 8.5 seems to be normal for surface waters. Dissolved solids measurements for the influent waters used for hydraulic fracturing (with additives) had a range of 200-800 mg/l, which is considered in the range of fresh surface water supplies. Interestingly, oil and grease measurements had a range of 17-22 mg/l and total organic carbon had a range of 124-143 mg/l; elevated values in these measurements may be due to various degrees of blending of reused waters into frac job influent water supplies.

Table 4-10: Summary of Chemical Characteristics of Influent Water Used for Hydraulic Fracturing after Additives were Blended

General Chemistry	LPG 3,4,X	LPG 1,2	Average	Units
pH	7.7	8.5		No Units
Acidity	ND	ND	ND	mg/L
Total Alkalinity	251	236	243.5	mg/L
Hardness as CaCO3	28	100	64	mg/L
Total Suspended Solids	360	80	220	mg/L
Turbidity	265	116	190.5	NTU
Chloride	151	21.6	86.3	mg/L
Total Dissolved Solids	800	203	501.5	mg/L
Specific Conductance	1550	484	1017	umhos/cm
Total Kjeldahl Nitrogen	36	21.9	28.95	mg/L
Ammonia Nitrogen	3.9	8	5.95	mg/L
Nitrate-Nitrite	0.048	0.036	0.042	mg/L
Nitrite as N	0.57	0.14	0.355	mg/L
Biochemical Oxygen Demand	130	245	187.5	mg/L
Chemical Oxygen Demand	829	559	694	mg/L
Total Organic Carbon (TOC)	143	124	133.5	mg/L
Dissolved Organic Carbon	84.3	281	182.65	mg/L
Oil & Grease (HEM)	22.2	17	19.6	mg/L
Cyanide, Total	ND	1.9	1.9	mg/L
Amenable Cyanide	ND	ND	ND	mg/L
Bromide	0.7	ND	0.7	mg/L
Fluoride	1.00	0.096	0.548	mg/L
Total Sulfide	ND	ND	ND	mg/L
Sulfate	107	28	67.5	mg/L
Total Phosphorus	3	0.11	1.555	mg/L
Total Recoverable Phenolics	ND	0.014	0.014	mg/L

Characteristics of flowback water sampled at 1 day and 10-12 days following the hydraulic fracturing event are presented in Table 4-11. The water is elevated in alkalinity with median values ranging from 725-1,200 mg/l. The water remains imbalanced with high levels of calcium and magnesium. Cations are dominated by sodium and calcium in this water. Anions are dominated by chloride. However, there is a fairly large sulfate component to the anionic balance, which has importance in the relative value of barium and strontium in the water. This topic is evaluated further in the discussion section.

Table 4-11: General Chemical Parameters, Barnett Day 1 and Day 3

General Chemistry Parameter	LPG1,2,3,X Day 1		LPG 1,2,3,4 Day 10-12		
	Range	Median	Range	Median	Units
pH	6.7 - 8	7.2	6.5 - 7.2	7.05	No Units
Acidity	ND	ND	ND	ND	mg/L
Total Alkalinity	482 - 1,590	980	215 - 1,240	725	mg/L
Hardness as CaCO3	840 - 2,800	2,200	3,500 - 21,000	5,800	mg/L
Total Suspended Solids	48 - 237	153	120 - 535	242	mg/L
Turbidity	37 - 266	130	144 - 314	239	NTU
Chloride	3,330 - 17,900	11,405	9,600 - 60,800	34,700	mg/L
Total Dissolved Solids	5,850 - 31,400	25,050	16,400 - 97,800	50,550	mg/L
Specific Conductance	11,300 - 59,000	55,550	34,800 - 179,000	111,500	umhos/cm
Total Kjeldahl Nitrogen	16 - 203	155	26 - 298	171	mg/L
Ammonia Nitrogen	9 - 223	186	18 - 486	303	mg/L
Nitrate-Nitrite	0.024 - 0.024	0.024	0.018 - 0.035	0.0265	mg/L
Nitrite as N	81.9 - 107	94.45	3.5 - 38.1	4.7	mg/L
Biochemical Oxygen Demand	89 - 1,480	311	101 - 2,120	582	mg/L
Chemical Oxygen Demand	850 - 4,280	1,485	927 - 3,150	2,945	mg/L
Total Organic Carbon (TOC)	34.7 - 99.1	47.5	6.2 - 36.2	9.75	mg/L
Dissolved Organic Carbon	30.6 - 91.3	53.55	5.5 - 65.3	11.2	mg/L
Oil & Grease (HEM)	5.6 - 1720	862.8	88.2 - 1430	163.5	mg/L
Cyanide, Total	15.6 - 15.6	15.6	6 - 6	6	ug/L
Amenable Cyanide	ND - ND	ND	ND ND	ND	mg/L
Hexavalent Chromium	0.014 - 0.16	0.0165	0.0085 - 0.11	0.071	mg/L
Dissolved Hexavalent Chromium	0.01 - 0.08	0.03	ND - 0.21	0.21	mg/L
Bromide	34.3 - 532	303.5	117 - 798	589	mg/L
Fluoride	1.6 - 30.6	4.75	3.5 - 12.8	3.8	mg/L
Total Sulfide	ND - ND	ND	ND - ND	ND	mg/L
Sulfate	259 - 972	669	120 - 1,260	709	mg/L
Total Phosphorus	0.37 - 3.4	0.79	0.19 - 0.7	0.395	mg/L
Total Recoverable Phenolics	0.034 - 0.45	0.08	0.0093 - 0.23	0.11965	mg/L

Volatile Compounds: The Barnett samples collected were analyzed for 70 volatile compounds of highly varied chemical characteristics, including the volatile hydrocarbon constituents that are normally found in produced water (such as benzene, toluene, ethylbenzene, and xylenes—or BTEX, and naphthalene) as well as constituents not known to be associated with conventional produced water such as chlorinated solvents and halogenated aromatics. The volatile organic content from the two raw water samples are presented in Table 4-12. Only traces of napthlene, toluene, and benzene were identified in the sample for Sites LPG 1 and LPG2.

Table 4-12: Volatile Organics in the Influent Water Samples

Volatiles (μg/L)	LPG 3,4,X	LPG 1,2	Average	Units
Naphthalene	ND	1.3	NA	μg/L
Benzene	ND	2	NA	μg/L
Toluene	ND	3	NA	μg/L

A summary of the results for volatile compound determinations performed recovered flowback water is shown in Table 4-13. Traces of benzene and other alkylated benzyl isomers were present in the recovered water. The relative concentrations did not appear to change with time after fracture and appeared to fluctuate fairly randomly. All data were, therefore, consolidated to present the range of results encountered in all 16 samples. It is important to note that of all the components measured in the test protocol, only 8 compounds common to waters generated from petroleum and gas sites were detected. No compound was observed in all 16 samples. The most commonly encountered materials were the BTEX and similarly related alkyl-benzene isomers. Traces of acetone, a commonly used cleaning fluid, were also found at measurable concentrations.

Table 4-13: Summary Volatiles Data; All Site Samples (Days 1-12, Total = 16 Samples)

Volatiles Data (μg/L)	Number of Observations	Range	Median	Average
Isopropylbenzene	2	0.8 - 69	35	35
Acetone	9	27 - 540	110	145
Naphthalene	12	8.3 - 84	22	27
1, 3, 5 - Trimethylbenzene	12	6.4 - 300	15	59
1, 2, 4 - Trimethylbenzene	13	6.9 – 1,200	37	173
Xylenes (total)	14	43 – 1,400	360	425
Benzene	15	49 – 5,300	680	1,198
Ethylbenzene	15	2.2 - 670	29	74
Toluene	15	79 – 8,100	760	1,246

The concentrations of 70 compounds were evaluated in the 16 test samples for a total of 1120 evaluations. Most tests were reported as non-detectable (1013 evaluations). Ninety-two observations were below 1 ppm and only 15 observations were above 1 ppm. Chlorinated, brominated, or other man-made compounds were not detected. More than 90 percent of all constituent determinations, on average, were at non-detectable levels and less than 1.5 percent of all constituent determinations were above 1 ppm (Figure 4-3).

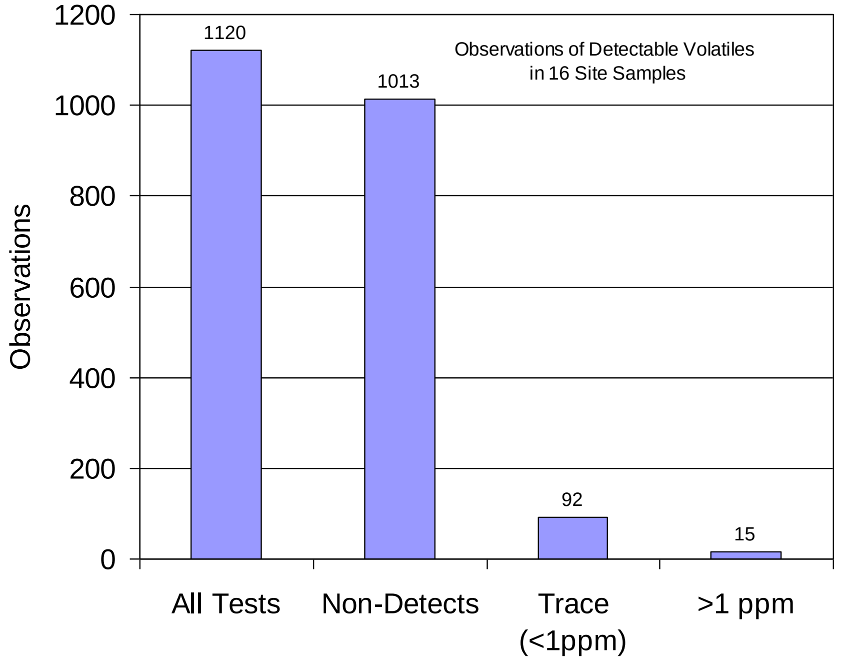

Figure 4-3: Number of Detectable and Non-Detectable Tests for Volatile Compounds

Semivolatile Compounds: A total of 112 semivolatile organic compounds were included in the analysis of influent water and in flowback water samples. A summary of the results of semivolatile determinations in the two raw water samples is presented in Table 4-14. The sample from Sites LPG 3, 4,and X had traces of PAH, and traces of two phthalate esters and two chlorinated hydrocarbons. Water from Site LPG 1 and 2 water had only a single report of pyridine.

Table 4-14: Semivolatile Compounds in the Influent Water Barnett Samples

Semi-Volatiles (µg/l)	LPG 3, 4, X	LPG 1,2	Average
Benzo (a) anthracene	1.3	ND	NA
Benzo (a) pyrene	1.1	ND	NA
Benzo (b) fluoranthene	1.3	ND	NA
Benzo (ghi) perylene	1.1	ND	NA
Benzo (k) fluoranthene	0.95	ND	NA
bis (2 - Ethylhexyl) phthalate	36	ND	NA
Butyl benzyl phthalate	2	ND	NA
Chrysene	1.2	ND	NA
Dibenz (a, h) anthracene	0.98	ND	NA
Di - n butyl phthalate	1.9	ND	NA
2, 6 - Dichlorophenol	2	ND	NA
Fluoranthene	1	ND	NA
Hexachlorobenzene	0.8	ND	NA
Indeno (1, 2, 3 - cd) pyrene	0.91	ND	NA
Pentachlorophenol	0.69	ND	NA
Phenanthrene	1.2	ND	NA
Pyrene	1	ND	NA
Pyridine	0.96	40	20.5

A summary of the results for semi-volatile compound determinations performed on the 16 site samples is shown in Table 4-15. Of the 112 compounds in the sample set, about 70% were not detected in any sample. Of the 32 compounds observed, about 1/3 of these were incidental detections in one of the 16 samples. All compounds detected are naturally occurring in petroleum. Pyridine is a nucleophile that is used widely in the manufacture of certain types of chemicals and pharmaceuticals and its presence may be due to its use as a precursor in the manufacture of one of the hydraulic fracturing additives. In general, nearly all of the semivolatile determinations were either non-detect (> 96% of the measurements) or at low trace levels (Figure 4-4).

Table 4-15: Semi-volatiles Data from 16 Site Samples (Days 1-23) All Five Sites

Semi-volatiles (µg/l)	Number of Observations	Range	Median	Average
Diphenylamine	2	0.6 - 10.0		5.3
Benzidine	1	ND - 35		
1, 4 - Dioxane	7	3.1 - 12	5.4	6.5
1, 2 - Diphenylhydrazine	2	0.5 - 7.8		4.2
Acetophenone	1	ND - 4.6		
Benzo (a) anthracene	1	ND - 17.0		
Benzo (a) pyrene	1	ND - 130.0		
Benzo (b) fluoranthene	2	0.5 - 84.0		42.2
Benzo (ghi) perylene	2	0.7 - 84.0		42.3
Benzo (k) fluoranthene	2	0.6 - 65.0		32.8
Benzyl alcohol	8	14.0 - 200	27.0	81.5
bis (2 - Ethylhexyl) phthalate	5	4.8 - 490	33	210
Butyl benzyl phthalate	4	1.9 - 110	12.6	34.3
Chrysene	2	0.57 - 240		120
Dibenz (a, h) anthracene	2	3.2 - 150		77
Di - n butyl phthalate	4	1.5 - 120	22	41
2, 4 - Dichlorophenol	1	ND - 15		
2, 4 - Dimethylphenol	8	8.3 - 21	15.5	14.5
Di - n - octyl phthalate	1	ND - 270		
Fluoranthene	1	ND - 0.18		
Fluorene	6	0.46 - 1.3	0.725	0.8
Indeno (1, 2, 3 - cd) pyrene	2	2.9 - 140		71
2 - Methylnaphthalene	16	5.4 - 20,000	22.5	1362
2 - Methylphenol	15	5.8 - 76	31	28.3
3 - Methylphenol & 4 - Methylphenol	15	7.8 - 100	44	41
Naphthalene	16	4.8 - 3100	22	238
N - Nitrosodiphenylamine	2	7.8 - 10		8.9
N - Nitrosomethylethylamine	1	ND - 410		
Phenanthrene	14	0.52 - 1400	1.3	107
Phenol	7	17 - 93	68	63
Pyrene	1	ND - 0.18		0.2
Pyridine	15	100 - 670	500	413

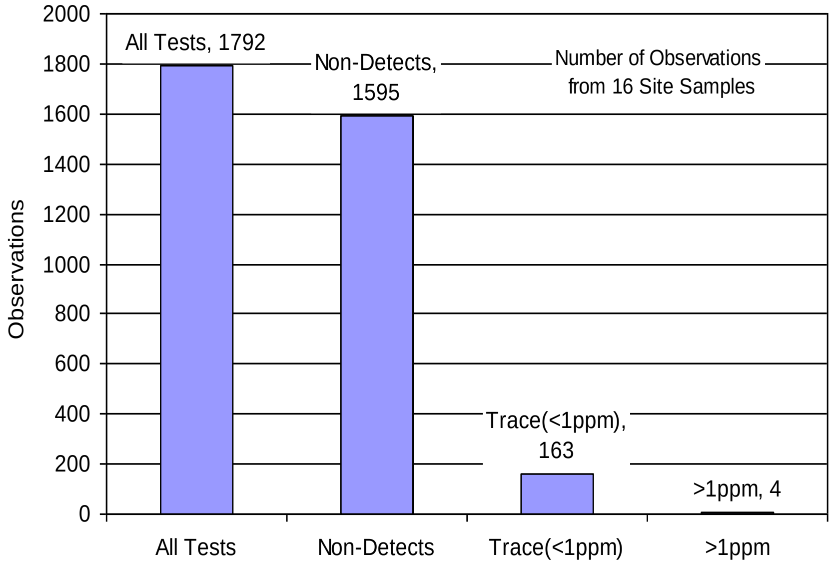

Figure 4-4: Distribution of Observations of Semivolatile Organics in 16 Barnett Site Samples

Pesticides: Determinations of the 20 chlorinated pesticides and 3 organophosphorus pesticides on 5 site samples and two source waters (Day 0) were performed. A single incidental measurement of less than 0.1 ppb was detected on day 1 from LPG 1. All other determinations for chlorinated pesticides were measured as non-detect. This would suggest that no chlorinated pesticides were introduced with the additives with the influent water during well completions.

Polychlorinated Biphenyls (PCBs): Determinations of the 7 polychlorinated biphenyl compounds (arochlors) were conducted on the two influent waters and Sites 2,4, and 5. All determinations for PCBs were measured as non-detect. This would suggest that no PCBs were introduced with the additives with the influent water during well completions. No PCBs were recovered in six samples recovered at three sites between days 1 and 7 after fracture.

Metals: Unlike the organic constituents, that do not change much with time, the metals concentrations tend to increase with time from fracture. A summary of metal concentrations in the two influent water samples is presented in Table 4-16. The total metals content of the Day 1 and Day 10-12 samples are summarized in Table 4-16. As seen in this table, sodium is the major cation in all of the samples, followed by concentrations in some samples of calcium, magnesium and barium that will need to be monitored for purposes of scale control in some locations.

Since strontium is present in flowback waters at concentrations between 345 to 4,830 mg/l in the 5-day flowback samples, it will be important for operators to implement procedures to prevent the formation of strontium-bearing scale. Iron levels in the range of 10 to 180 mg/l may also need to be watched and mitigated in order to prevent operational difficulties at a number of well completion locations. Heavy metals of toxicological concern that are often associated with urban industrial activity (including chromium, copper, nickel, zinc, lead, cadmium, mercury and arsenic) are at very low levels in all of the shale gas water samples.

Table 4-16: Total Metals in Influent Water Samples

Total Metals	LPG 3,4,X	LPG 1,2	Average	Units
Aluminum	0.525	0.604	0.564	mg/L
Antimony	ND	ND		mg/L
Arsenic	ND	ND		mg/L
Barium	0.0527	2.66	1.356	mg/L
Beryllium	ND	ND		mg/L
Boron	0.509	0.124	0.317	mg/L
Calcium	13.1	17.1	15.1	mg/L
Cadmium	ND	ND		mg/L
Cobalt	ND	ND		mg/L
Chromium	ND	0.0064	0.0064	mg/L
Trivalent Chromium	ND	0.0026	0.0026	mg/L
Copper	ND	ND		mg/L
Iron	1.68	1.18	1.43	mg/L
Lead	0.0127	ND		mg/L
Lithium	0.0464	ND		mg/L
Magnesium	1.57	11.5	6.535	mg/L
Manganese	0.0359	0.0478	0.042	mg/L
Molybdenum	ND	ND		mg/L
Nickel	ND	ND		mg/L
Potassium	3.5	4.46	4	mg/L
Sodium	278	81.3	179.6	mg/L
Selenium	ND	ND		mg/L
Tin	ND	ND		mg/L
Strontium	0.244	1.3	0.77	mg/L
Titanium	ND	ND		mg/L
Thallium	ND	ND		mg/L
Zinc	0.0281	ND		mg/L
Mercury	ND	ND		mg/L

Table 4-17: Metals Data in the Barnett Samples

Metals Data (mg/l)	LPG1,2,3,X Day 1		LPG 1,2,3,4 Day 10-12	
	Range	Median	Range	Median
Aluminum	0.114- 0.572	0.495	0.37 - 2.21	0.43
Antimony	ND	ND	ND	
Arsenic	ND	ND	ND	
Barium	0.053 - 3.31	1.50	0.93 - 17.9	3.6
Beryllium	ND	ND	ND	
Boron	0.51 - 39.1	23.5	7.0 - 31.9	30.3
Calcium	13 - 768	564	1,110 - 6,730	1,600
Cadmium	ND -	0.000	ND	
Cobalt	0.006 - 0.028	0.014	0.01 - 0.01	0.01
Chromium	0.011 - 0.066	0.030	0.01 - 0.12	0.03
Trivalent Chromium	0.003 - 0.014	0.008	ND 0.03	0.01
Copper	0.087 - 0.131	0.109	0.06 - 0.52	0.29
Iron	ND		12.1 - 93.8	24.9
Lead	0.013 - 0.034	0.013	0.01 - 0.02	0.02
Lithium	0.046 - 10.8	9.01	2.56 - 37.4	19.0
Magnesiium	2 - 116	89	149 - 755	255
Manganese	0.036 - 1.98	0.711	0.25 - 2.20	0.86
Molybdenum	0.015 - 0.066	0.043	0.02 - 0.03	0.02
Nickel	0.029 - 0.036	0.033	0.03 - 0.05	0.04
Potassium	4 - 216	111	80 - 750	316
Sodium	278 - 12,200	7805	4,370 - 28,200	18,850
Selenium	ND		0.03 - 0.04	0.03
Tin	0.004 - 0.004	0.004	ND	
Strontium	ND - 206	132	48 - 1,550	529
Titanium	ND		0.02 - 0.03	0.02
Thallium	ND		ND - 0.14	
Zinc	0.028 - 0.560	0.202	0.10 - 0.36	0.15
Mercury	ND		ND	

Deliverables

Topical Report: Hayes, T.D., and Severin, B.F., (2012) Characterization of Flowback Waters from the Marcellus and the Barnett, RPSEA Report No. 08122-05.09.

Completed Manuscripts to be Submitted to SPE for Publication in 2012:

Severin B.F., Galusky, L.P and Hayes, T.D., Empirical Interpretation of Barnett and Marcellus Flowback Events: Part I, Hydraulic Considerations

Severin B.F., Galusky, L.P and Hayes, T.D., Empirical Interpretation of Barnett and Marcellus Flowback Events: Part II, Brine Profiles

Severin B.F., and Hayes, T.D., Empirical Interpretation of Barnett and Marcellus Flowback Events: Part III, Projection of Wellhead Profiles

Impact to Producers

An understanding of the composition of flowback and produced waters is a highly important body of information to the development of strategies for near term and long term management. Furthermore, the work started by the GTI project in measuring the profiles of flow and salt output from wells in the Marcellus and Barnett is critical to modeling and predicting water management issues associated with shale gas plays. The overarching goal of this project is to provide the producers with information that helps to 1) minimize fresh water utilization, 2) maximize water reuse, 3) minimize disposal costs, and 4) reduce truck traffic (carbon footprint) throughout a gas play. The major implication of this work is the development of a database from which water management and water treatment options may be rationally implemented.

Conclusions and Recommendations

Implications

Measurements on water composition taken in the Marcellus and Barnett plays clearly show that the monitoring of waters can be greatly simplified to a small fraction of the parameters measured in the project. Since chlorinated hydrocarbons were at or near non-detect levels, it does not make sense to specify any of this category for future water composition work; this could save the industry more than 80 percent of the analysis costs. This is also true for PCB's, pesticides and organopesticides which are also at non-detect levels. Monitoring costs can be greatly reduced by making this simplification.

Non-radioactive heavy metals are also at demimus levels, about 3-4 times lower in concentration than metals levels found in sewage sludges. The only metals that need to be measured are those few constituents that form scale (such as calcium, magnesium, iron and barium). Accordingly, metals analysis does not need to include an exhaustive list. This category of analysis can be greatly simplified.

The data from this effort have implications concerning how flowback waters can be managed. Conventional treatment needs may be estimated from parameters such as biological oxygen demand, total carbon, total kjdehal nitrogen, oil and greases, etc. The following two plots show the median observed conventional pollutants for the Marcellus samples (Figure 4-5) and for the Barnett samples (Figure 4-6).

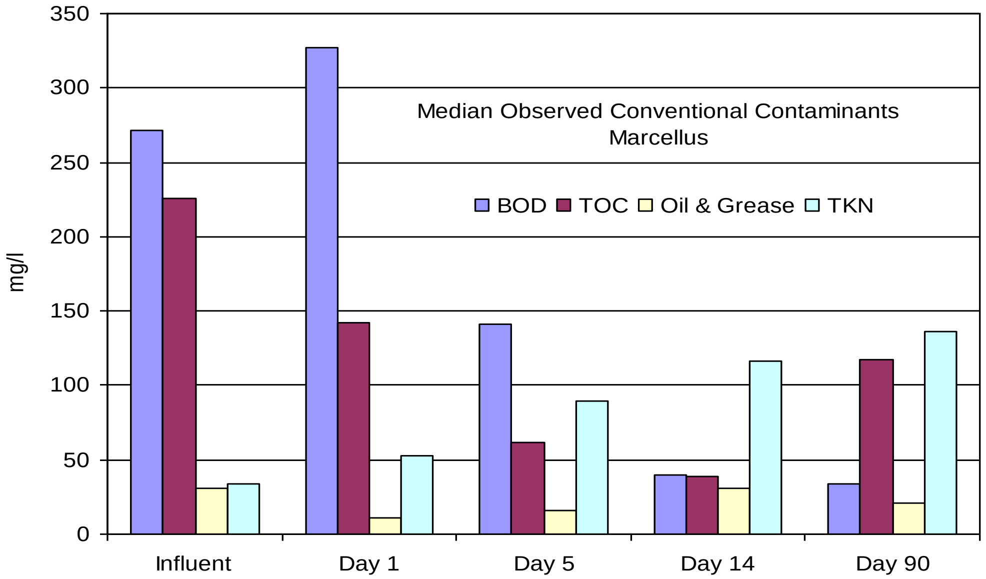

Figure 4-5: Median Conventional Components of Flowback Water from the Marcellus Samples

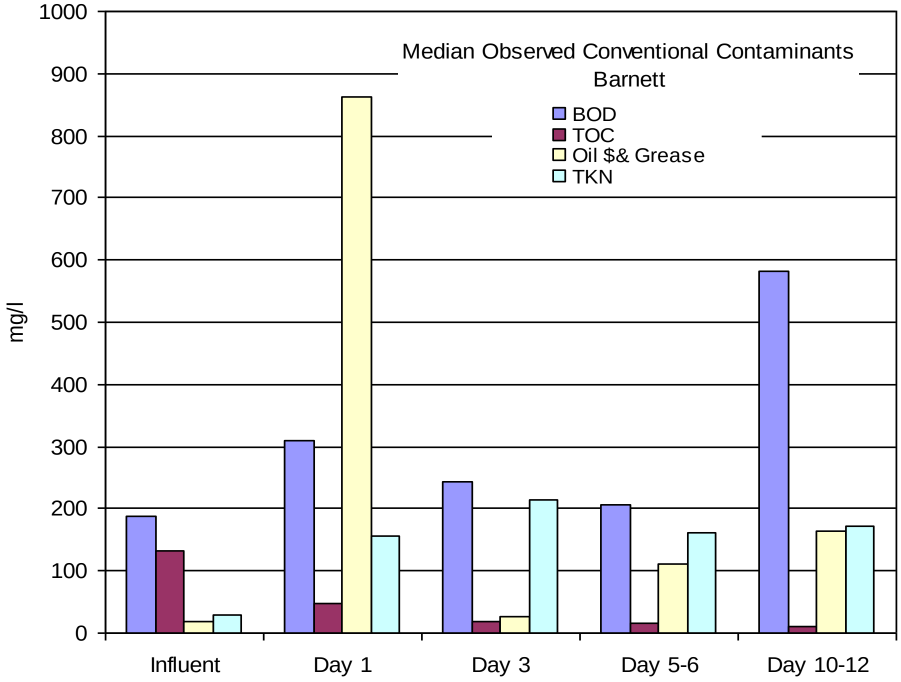

Figure 4-6: Median Observations of Conventional Contaminants in the Barnett Samples

Heavy metals of toxicological concern that are often associated with urban industrial activity (including chromium, copper, nickel, zinc, lead, cadmium, mercury and arsenic) are at very low levels in all of the shale gas water samples compared to levels reported for municipal wastewaters. Table 4-18 presents median values from the 5-Day Marcellus flowback samples compared to median heavy metals concentrations measured in sewage sludges (biosolids) generated by Penn State for the State of Pennsylvania (Stehouwer, 2000). The comparison shows that the levels of heavy metals of concern are 100 to 10,000 times higher in municipal biosolids (sewage sludges that are routinely transported across communities to disposal sites) than the levels measured in shale gas waters.

Table 4-18: Comparisons of Median Metals Levels in Shale Gas Waters with Municipal Biosolids (Sewage Sludge)

Metal	5-day Flowback	Sewage Sludge*	Units
Chromium	0.015	35	mg/l
Copper	0.029	511	mg/l
Nickel	< 0.0004	22.6	mg/l
Zinc	0.156	705	mg/l
Lead	< 0.0021	65	mg/l
Cadmium	< 0.0001	2.3	mg/l
Mercury	<0.0002	1.5	mg/l
Arsenic	0.029	3.6	mg/l

* Penn State study reporting median heavy metal content values for Pennsylvania publicly owned treatment works (POTW) biosolids. Stehauwer, et al., 2000.

The tendancy for the flow rate to decrease, and the total dissolved solids content to increase with time, provides opportunity to capture and reuse early flowback for reuse. The major challenge to the realization of this opportunity is the ultra-high concentration of divalent cations, which have tendencies to cause precipitates and scale in process equipment. The seven major cations encountered in the flowback waters are sodium, calcium, strontium, potassium, magnesium, iron, barium, and lithium. Of these cations; calcium, barium, strontium, magnesium, and iron are notorious scale formers. The seven major anions measured in these waters are chloride, bicarbonate, bromide, fluoride, sulfide, sulfate, and phosphate. Of these anions, carbonate species, sulfate, and phosphate are known to be potential scale formers. Likewise, sulfate is biologically active, being reduced to either sulfur or hydrogen sulfide.

Figure 4-7 is a distribution profile of the relative abundance of the major cations in all samples from the Marcellus and the Barnett. Figure 4-8 is a distribution of the relative abundance of the anions. The calculation for these figures was as follows. Most of the cation charge is carried by sodium. The proportion of sodium (87% of cation equivalents) in the Barnet samples is somewhat higher than the Marcellus samples (74% of cation equivalents). Chloride is the most common anion, representing more than 93% of the anionic content in the Barnett and 99% in the Marcellus samples. Sodium and Chloride are not shown in Figure 4-8 in order to better observe the trends in the less concentrated species.

Calcium is the second most abundant cation, representing about 22% of the cationic charge in the Marcellus and about 9% in the Barnett samples. This difference may, in part be due to the relatively higher content of carbonate alkalinity in the Barnett than in the Marcellus. Calcium also precipitates as a sulfate. The relative sulfate concentration in the Barnett 30 times greater than in the Marcellus. This also suggests a reasonable expectation why the calcium in the Barnett is less abundant than in the Marcellus samples. Calcium is stable at pH< 6. One potential means of handling calcium is by addition of acid to stabilize the calcium. The modest bicarbonate concentration in both sample bases indicates that there is a relatively low buffering capacity. A small acid addition should be sufficient to perform this procedure.

Strontium carries 1-2 % of the cationic charge in the flowback waters. Strontium is known to co-precipitate with calcium and barium, either as a carbonate or a phosphate, or a sulfate. Any pretreatment or reuse option should be designed to handle strontium.

Iron (calculated herein as the ferrous form) will precipitate at pH 5 as a hydroxide. With oxygen present, iron will convert to the ferric form and more readily precipitate at lower pH. A standard means of controlling iron is aeration followed by caustic addition and settling. Iron is also biologically active, inviting many different types of surface active bacteria that catalyze many redox reactions. These reactions may involve oxygen, carbonate, organic carbon, sulfate, sulfur, and sulfide.

Barium readily precipitates as a sulfate. It is interesting to note that the Barnett water contains much more sulfate than the Marcellus water. This may be one reason why the barium content of the Barnett water has relatively less barium than the Marcellus water.

Potassium is the fourth most abundant cation, but should not pose any treatment problems. Magnesium is about as abundant as potassium. Magnesium precipitates at high pH (>11) as a hydroxide, or in phosphate and ammonia rich waters as struvite. These conditions will not likely be found in these waters. Lithium is present in these waters, but should not interfere with any treatment process.

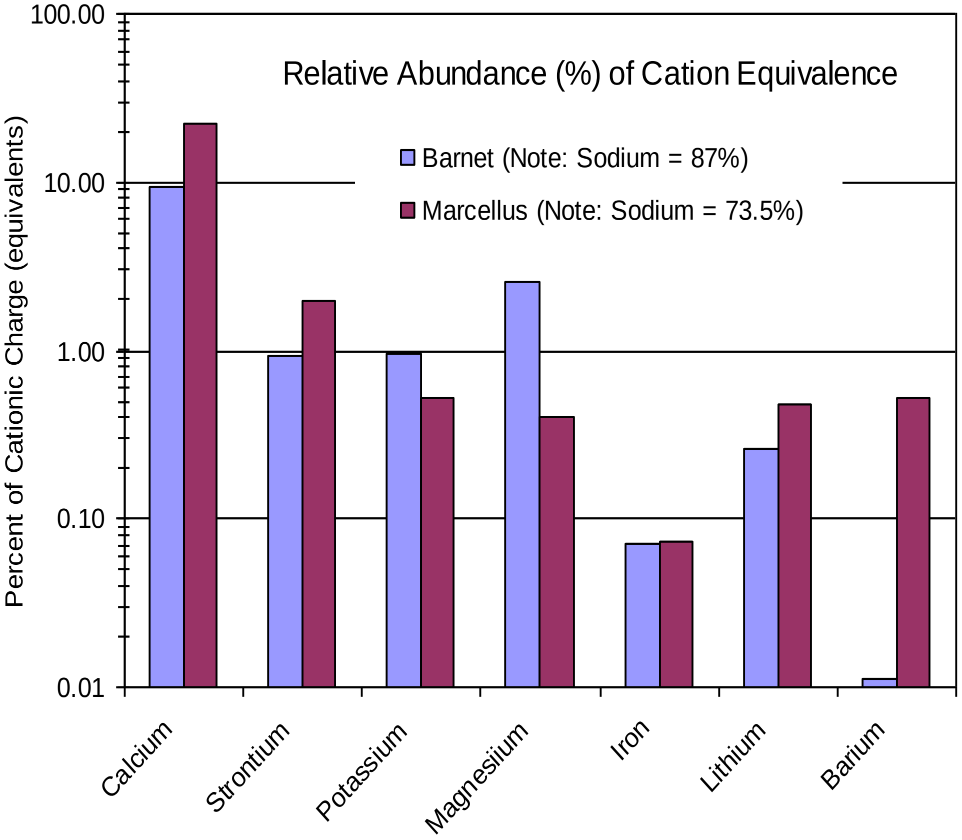

Figure 4-7: Relative Abundance of Cations in Flowback Waters

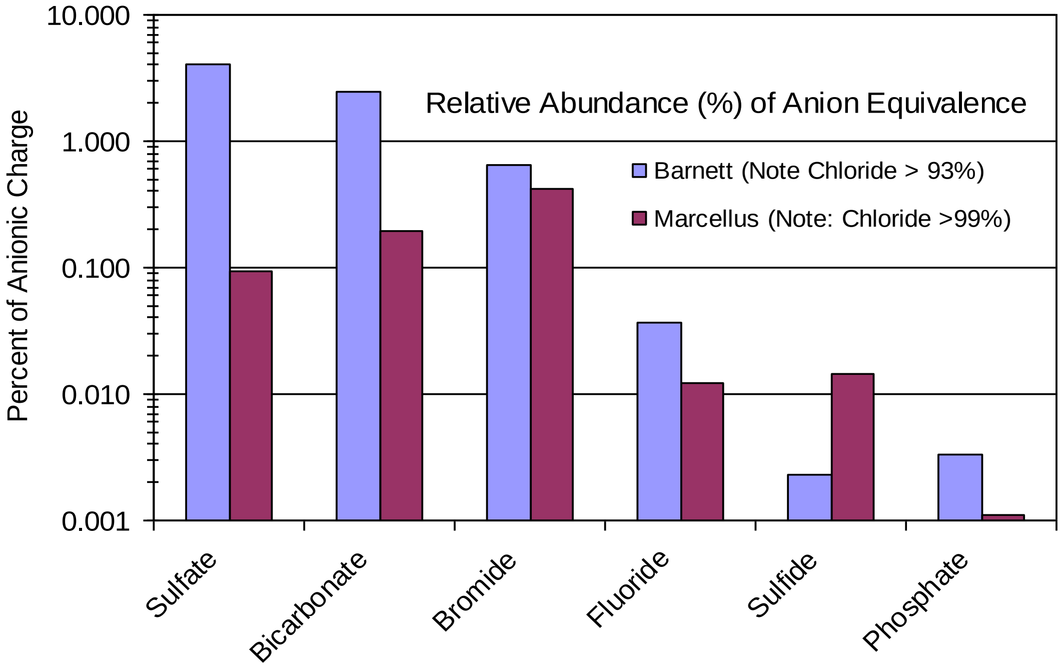

Figure 4-8: Relative Abundance of Anions in Flowback Waters

Outlook

The comprehensive chemical data sets from the Marcellus and Barnett provide an opportunity to rationally discuss water management issues within these two geographic regions. Important observations on the presence and absence of certain classes of compounds will guide discussions of permitting, and compliance testing, reuse, and treatment options. These observations will also guide data base generation within other shale gas regions, such as the Eagle Ford.

Value

The results of this effort strongly suggest that monitoring of constituents of significance and/or of concern can be greatly simplified; if this can be done, sampling and analysis costs can be reduced by more than half without posing significant risk to human health or the environment. In addition, the value of this development effort was to open a new dialogue concerning the long term water management issues facing the development of shale gas plays. These data establish trends in the chemical nature of flowback waters. Most notably, heavy metal contamination is minimal. The major classes of recovered organic matter include some of those input as additives (such as acetone, pyridine, and phthalate esters) and the classic contaminants encountered in the petroleum and gas industries (PAHs, and BTEX). These are fairly typical wastewater components and do not present treatment problems. The major challenge appears to be the presence of high concentrations of divalent cations. Segregation and treatment options for these salt components are presented in other sections of this report (Task 5 Feasibility of Early Flowback Capture, Task 7 Mechanical Vapor Recompression, Task 8 Electrodialysis, and Task 10 Field Experiment on Coated Membranes).

Future Considerations

The testing and quality plans developed for this project may be easily duplicated for the collection of other databases for other geographic regions. More likely, however, these results will guide the streamlining and focusing of data collection in future sites.

References

Stehouwer, R.C., A.M. Wolf, and W.T. Doty. 2000. "Chemical Monitoring of Sewage Sludge in Pennsylvania: Variability and Application Uncertainty." J. Environ. Qual. 29: 1686–1695.

Hayes, T.D. 2009. Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas, Final Report to the Marcellus Shale Coalition. Gas Technology Institute, Des Plaines, Il.

5 Feasibility of Early Flowback Capture

Rationale

Fresh water is critical for natural gas production in the Barnett Shale, where in excess of 1 to 5 million gallons are required for the completion of each gas well. The financial costs, logistical challenges and public relations concerns over the use of fresh water supplies thus impel Barnett gas producers to use less fresh water and to use it more efficiently. One source of relatively fresh water is represented by the early flowback waters recovered during the first few days after each hydraulic fracture. Methods for predicting the recovered volume and salt concentrations are needed in order to better plan for the best use of this type of water.

Objective

The objectives of this work were to develop a simple, empirical modeling approach for characterizing and forecasting flowback water rates and total dissolved solids (TDS) and to use such models to characterize the efficacy of flowback water recycling based on predefined TDS reuse criteria. A simple flowchart is presented to demonstrate one approach to the separation and segregation of flowback waters based on conductivity.

Goals

As the project developed, the specific goals were refined and refocused to develop a general engineering analysis and complimentary computer model for the newly collected Barnett database, as well as an existing Marcellus database. Specific goals included the following:

1. Collect timed flowback recovery and salt concentration data for a series of well completions in the Barnett.
2. Determine underlying trends in the data, and develop a general hydraulic model.
3. Develop a simplified flow sheet to take advantage of flow segregation.

Approach

Hayes (2009) presented some of the first data collected on flow and salt profiles of flowback water from the Marcellus (Appalachian area, Pennsylvania and West Virginia) formation. The volume of flowback collected on calendar days 1, 5, 14, and 90 after the fracture event were collected from 19 wells. Two important conclusions concerning the hydraulics were discovered from these data.

1. The ultimate recovery of water is less than 35% of the initial charge on a weighted basis of flow from all wells.
2. The flow rate from the wells decreases rapidly with time, such that most of the water (80%) is collected within the first 14 days after fracture. Usually, less than 20% of the flowback water is recovered between days 15 and 90.

Galusky and Hayes (October 2011) presented data from eleven shale gas well hydraulic fracturing events in the Barnett shale region. Figures in the Gausky and Hayes report were analyzed and representative data were tabulated for the current summary. These data include daily flow rates data and cumulative flow. These data suggested similar immediate conclusions to those described in the previous Hayes (2009) report. The combined information in Hayes

(2009) and Galusky and Hayes (October 2011) allow for a deeper understanding the flowback events from two different geographic regions.

Summary of the Hydraulic Model: The hydrofracture event (Severin, et al. 2012a) is presented as follows. A total volume of up to three hundred thousand barrels, V_F (Fracture Volume, barrels) is expended down-hole. A certain amount of this water, V_U (Unrecovered barrels) is unrecoverable. This leaves a potential volume available for recovery, V_A (Available barrels):

1) $V_F = V_U + V_A$

The available volume is recovered over a period of time, T (days). As time approaches a long period, typically 90 to 120 days, then the volume recovered, V_R (recovered barrels) approaches the available volume, V_A:

$$V_R \Rightarrow V_A \ as \ T \Rightarrow 90 \ to \ 120 \ days$$

The rate of flowback recovery, Q (Barrels/day), is by definition,

2) $Q = \frac{dv_R}{dt}$

where v_R is the recovered flowback volume. If the available volume for recovery is viewed as a reservoir of fluid under pressure, and if the pressure is relieved by the release of fluid, then simple Darcy kinetics may be envisioned. As written for this presentation, where k_1 (per day) is a first order rate coefficient:

3) $\frac{dv_R}{dt} = k_1 (V_A - v_R)$

This suggests in general terms, that there is an unknown empirical relationship between the rate of flowback recovery and the driving force for recovery, where (V_A-v_R) is used as a surrogate for pressure differential.

The cumulative volume of recovered flowback water is the integral over time, T, which is immediately recognized as the asymptotic exponential function.

4) $V_R = V_A \left(1 - e^{-k_1 T}\right)$

The site data from the Barnett included both hydraulic rate data and cumulative volume data. Equation 3 indicates that rate data should correlate linearly with cumulative volume, with the slope = -k_1, and the X-intercept = V_A/k_1. Table 5-1 summarizes the results of the linear analysis for ten Barnett sites. LPG9 had insufficient data for this detailed analysis.

Table 5-1: Regression Results for First Order Rate Approximation; Barnett

Site	VF Total Fracture Volume (bbl)	V_A Recovered Volume (bbl)	k_1 (day^{-1})	r^2
LPG1	198,760	75,900	0.029	0.953
LPG2	183,750	28,300	0.043	0.965
LPG3	237,040	46,100	0.026	0.973
LPG4	64,050	20,700	0.030	0.929
LPG5	120,890	45,500	0.027	0.961
LPG6	170,900	53,100	0.018	0.915
LPG7	100,610	33,900	0.084	0.984
LPG8	155,360	33,000	0.062	0.938
LPG10	239,230	56,400	0.027	0.967
LPG11	140,700	51,900	0.017	0.971

The site data from the Marcellus included cumulative volumes as a function of time at days 1,5,14, and occasionally 90 days after fracture. Data from the Marcellus were from six vertical wells (Table 5-2) and seven horizontal wells (Table 5-3). Equation 4 demonstrates the expected relation between the kinetic coefficient and recovered volume from cumulative flow data. Tables 5-2 and 5-3 present the results of this analysis for the twelve Marcellus sites. Due to the relatively few data points, regression coefficients were not calculated.

Table 5-2: Fitted Model Parameters from 6 Vertical Sites in the Marcellus

	Fracture Water	Flowback Recovered (bbl) Days after Fracture				Model Fitted	
						Available volume	First Order Coefficient
Site	V_F (bbl)	1	5	14	90	V_A (bbl)	k_1(day^{-1})
A	40,046	3,950	10,456	15,023		16,100	0.21
B	94,216	1,095	10,782	13,718	17,890	18,100	0.13
H	36,035	3,988	16,369	21,282		22,500	0.23
N	11,435	2,432	2,759	3,043	3,535	3,600	0.18
Q	23,593	1,315	3,577	5,090		5,500	0.24
S	16,460	2,094	7,832	9,345	10,723	10,800	0.21

Table 5-3: Fitted Model Parameters from 7 Horizontal Sites in the Marcellus

	Fracture Water	Flowback Recovered (bbl) Days after Fracture				Model Fitted	
						Available volume	First Order Coefficient
Site	V_F (bbl)	1	5	14	90	V_A (bbl)	k_1(day^{-1})
C	146,226	3,308	9,652	15,991		18,900	0.14
D	21,144	2,854	8,077	9,938	11,185	11,300	0.15
E	53,500	8,560	20,330	24,610	25,680	25,800	0.26
F	77,995	3,272	10,830	12,331	17,413	17,700	0.12
G	123,921	1,219	7,493	12,471	31,735	33,000	0.09
M	99,195	16,419	17,935	19,723		20,500	0.45
K	70,774	5,751	8,016	9,473		11,000	0.20

There are insufficient data in the hydraulic databases to discern any correlations between fracture volume, recovered volume, or the kinetic coefficient. Recovered volume versus fracture volume, percent recovery versus fracture volume, and kinetic coefficient versus fracture volume all appear to be random populations. There also did not appear to be any significant differences between horizontal and vertical wells in the Marcellus data.

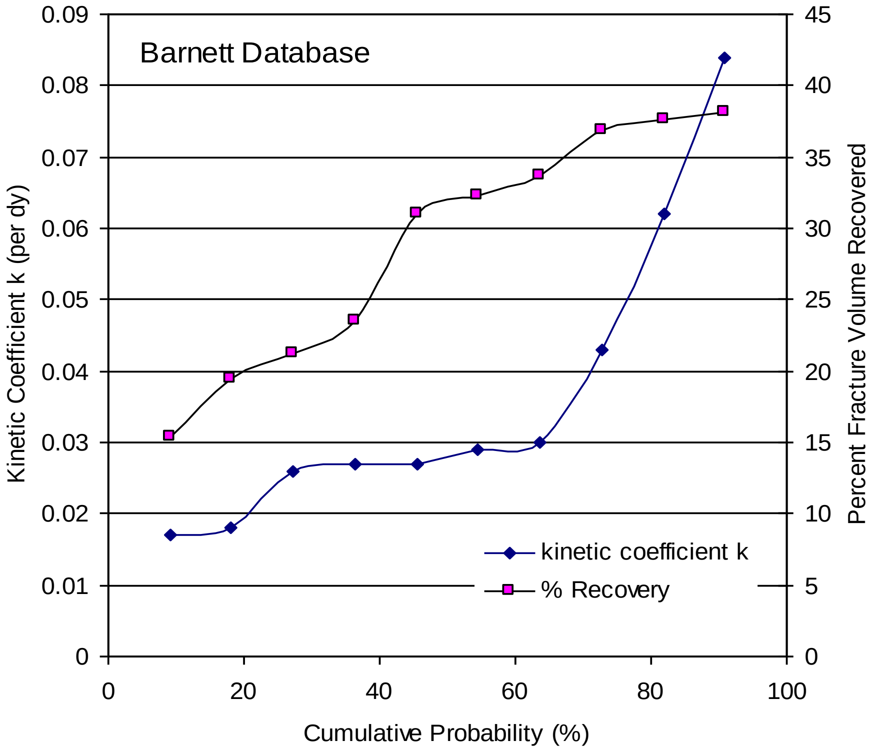

Figure 5-1: Cumulative Probability Plot for the Kinetic coefficients and Percent Water Recovery for the Barnett Database

Hydraulic data were, therefore, analyzed as independent, random variables. Figure 5-1 shows the Barnett kinetic coefficients and percent water recovery databases (from Table 5-1) as cumulative probabilities. Figure 5-2 gives a similar analysis for the Marcellus database. Table 5-4 is a summary of the average and standard deviations of the hydraulic parameters for the databases (Tables 5-1 and 5-2).

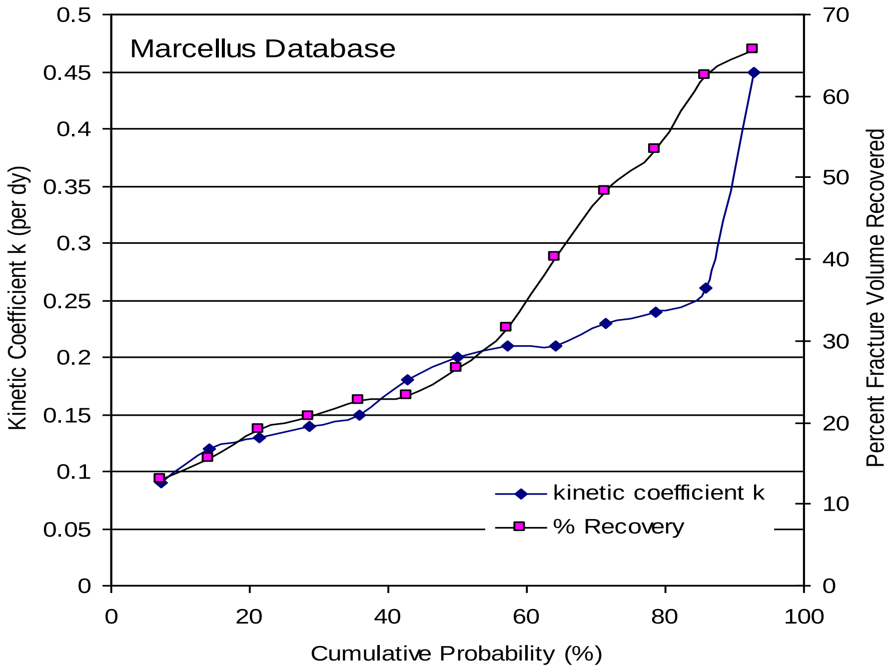

Figure 5-2: Cumulative Probability Plot for the Kinetic coefficients and Percent Water Recovery for the Combined Marcellus Database (Horizontal and Vertical Drilling).

Table 5-4: Summary of Hydraulic Parameters for the Barnett and Marcellus Databases

	n	k (day^{-1})	Standard Deviation k	Recovery %	Standard Deviation %
Barnett	10	0.04	±0.021	28.9	±8.3
Marcellus vertical	6	0.20	±0.040	40.4	±19.7
Marcellus horizontal	7	0.20	±0.123	28.6	±15.9
Marcellus combined	13	0.20	±0.091	34.0	±18.1
n = samples in database					

Summary of the Concentration Profiles: Cumulative flow and wellhead concentrations for twelve of the thirteen Marcellus sites and six of the Barnett sites were previously presented (Severin et al., 2012b). Most data sets show a rapid rise in the wellhead concentrations between days 1 and the final day of recorded data. Figure 5-3 is an example of data from six sites in the Marcellus showing a typical relationship between the wellhead concentration, C_W (mg/l) and recovered volume, V_R. Data correlate well to an exponential model. In this equation, the constant (a) has units (mg/l) and (b) has units (barrels).

5) $C_W = ae^{bV_R}$

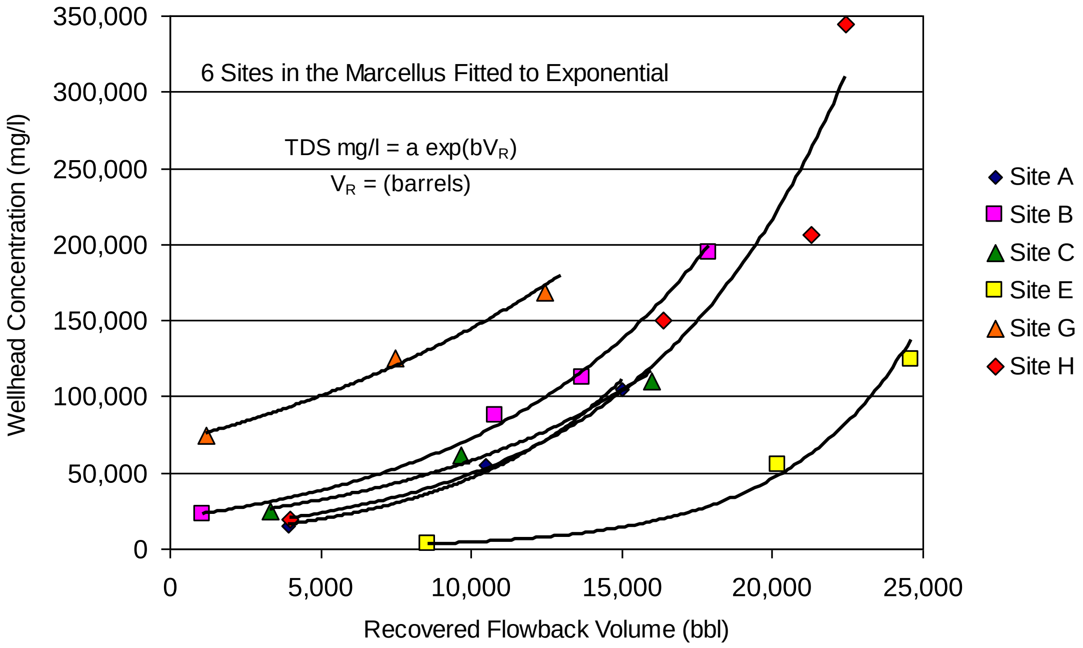

Figure 5-3: Wellhead Concentrations versus Recovered Volumes for Six Sites in the Marcellus Fitted to Exponential Curve

A summary of the concentration coefficients are presented in Table 5-5 (Barnett) and Table 5-6 (Marcellus). No mechanistic explanation can presently be made to rationalize the good fit to the exponential curve; this is simply an empirical observation. However, the parameters in the exponential equation have physical meaning. The constant *a*(mg/l) closely represents the concentration at the wellhead on day zero, C_0(mg/l). The constant *b*(barrels^{-1}) represents a characteristic volume at a representative concentration. All of the curves trend toward a concentration that cannot exceed the background concentration, C_S (mg/l). Therefore, the characteristic volume, *b*, approaches a value approximately near the end of the recoverable fluid, V_A.

Table 5-5: Fitted Concentration Profile Parameters From Six Sites in the Barnett

Site	a (mg/l)	b (bbl^{-1})	r^2
LPG1	32,970	1.7 x 10-5	0.86
LPG2	19,750	8.6x 10-5	0.93
LPG3	12,800	5.4x 10-5	0.93
LPG7	11,500	5.3 x 10-5	0.87
LPG10	45,600	2.2 x =10-5	0.90
LPG11	45,000	2.8x 10-5	0.80

Table 5-6: Concentration Profile Coefficients From 12 Sites in the Marcellus

Site	a (mg/l)	b (bbl^{-1})	r^2
A	7,500	0.000185	>0.98
B	23,658	0.000117	0.98
C	2,250	0.000254	0.98
D	1,889	0.0004	0.98
E	500	0.000228	0.98
F	43,800	0.0001	0.97
G*	*61,000*	*0.000049*	
H	8,500	0.000165	0.97
K	*2,765*	*0.00033*	
N	700	0.00165	
Q	2,100	0.00079	0.96
S	225	0.00065	0.98
*G parameters set to not exceed 270,000 mg/l on or before day 90			

Equation 5 is further developed to compute the total salt mass, M (lbs), or the average concentration, C_{avg} (mg/l), for any partial volume, from V_R from V_1 to V_2 (bbl), during the recovery period as shown in Equations 6 and 7. The constant, $F_X = 0.0035$, is the conversion factor from mg/l to pounds per barrel.

$$6)\ M = F_x \int_{V_1}^{V_2} C_W dv_R = F_X \frac{a}{b}(e^{bV_2} - e^{bV_1})$$

$$7)\ C_{avg} = \frac{\int_{V_1}^{V_2} C_W dv_R}{\int_{V_1}^{V_2} dv_R} = \frac{a}{b}\frac{\left(e^{bV_2} - e^{bV_1}\right)}{\left(V_2 - V_1\right)}$$

By example, Figure 5-4 shows projections for total salt production at seven sites in the Marcellus from day 1 ($V_1 = 0$) projected out to 90 days. The curves were generated using the fitted parameters in Table 5-5 and the integrated mass equation with $V_1 = 0$

$$8)\ M = F_x \int_{V_1=0}^{V_2} C_W dv_R = F_X \frac{a}{b}(e^{bV_2} - 1)$$

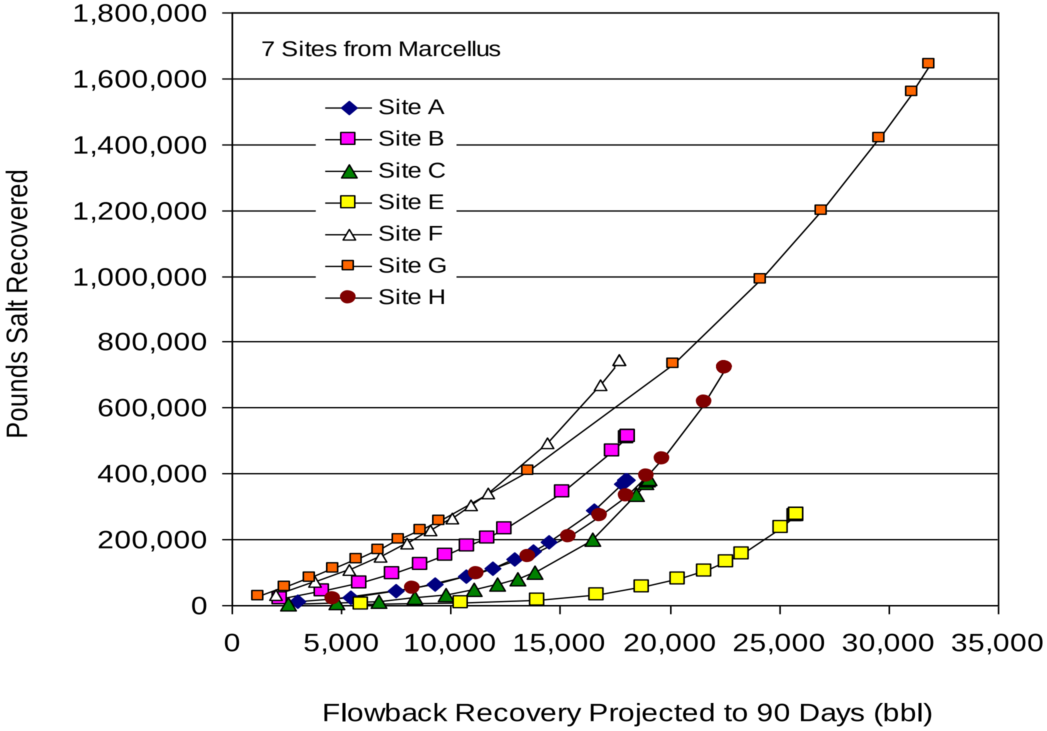

Figure 5-4 Model Projected Salt Generation at Seven Marcellus Sites

Deliverables

Topical Reports

Galusky, L.P,Jr., and Hayes, T,D., (August 2011) Feasibility and Design Approach for Automated Classification and Segregation of Early Flowback Water for Reuse in Shale-Gas Hydraulic Fracturing, Barnett and Appalachian Shale Water Management and Reuse Technologies, Report 08122-05-06, RPSEA Contract 08122-05

Galusky, L.P,Jr., and Hayes, T,D., (October 2011) Feasibility Assessment of Early Flowback Water Recovery for Reuse in Subsequent Well Completions, Barnett and Appalachian Shale Water Management and Reuse Technologies, Report 08122-05.07, RPSEA Contract 08122-05

Completed Manuscripts to be Submitted to SPE in 2012

Severin, B.F., Galusky, L.P,Jr., and Hayes, T,D., (2012a) Empirical Interpretation of Barnett and Marcellus Flowback Events: Part I, Hydraulic Considerations

Severin, B.F., Galusky, L.P,Jr., and Hayes, T,D., (2012b) Empirical Interpretation of Barnett and Marcellus Flowback Events: Part II, Brine Profiles

Severin, B.,F, and Hayes, T.D., (2012c) Empirical Interpretation of Barnett and Marcellus Flowback Events: Part III, Projection of Wellhead Profiles

Hayes, T.D., and Severin, B.F., (2012) Empirical Interpretation of Barnett and Marcellus Flowback Events: Part IV, Life Cycle Projection of a Marcellus Play

Conclusions and Recommendations

Impact to Producers**:** The empirical hydraulic and concentration profiles presented in Equations 3, 4, 5, 6, 7 and 8 may be utilized, along with the hydraulic databases in Figures 5-1 and 5-2, to make engineering and management projections for flowback events from planned fracture events. Figure 5-5 shows the projected relation of rate of flowback recovery and cumulative flowback volume as a function of pumping days after fracture for the median Barnett event. These curves show the characteristic rapid decrease in flowback rate during the initial recovery period and the asymptotic approach to a final volume. Figure 5-6 shows the projected relation between the total mass of salt recovered, the wellhead concentration and the impoundment concentration as a function of the recovered volume for the median Barnett event.

Value: Simple mathematical relations between brine concentrations and flowback recovery have been developed for preliminary databases for the Barnett and the Marcellus. It is telling that both data sets follow the same trends, possibly leading to a better understanding of the mechanisms of flowback. These simple tools may be immediately employed in site projection, management, and form a preliminary tool for future database generation and analysis.

One current management strategy for flowback control is to hold the water down-hole for extended periods of time. In the Barnett, the goal is a water retention strategy aimed at saving water for reuse in the next fracture. In the Marcellus, this strategy is employed in an attempt to dissipate the water to minimize the recovered volume. In either case, there is a concern that holding the water down-hole for extended periods will increase the concentration of the flowback water by dissolution of subsurface salts. This investigation partially addresses these questions.

Equations 2 and 3 are based on the concept that the rate of flowback is dependent on the recovered volume. In the initial data set for the Barnett (Galusky and Hayes, T,D., 2011) three sites were described that had were subjected to shut-in periods of up to 65 days. The analysis of these data with the present model (Severin et al. 2012a) indicated that the shut-in period did not influence the recovery rate. The data suggest that the rate of flowback is more dependent on the total volume of recovered water than on the time of recovery. Recovery shutdown periods of up to 65 days had little bearing on the kinetics of recovery.

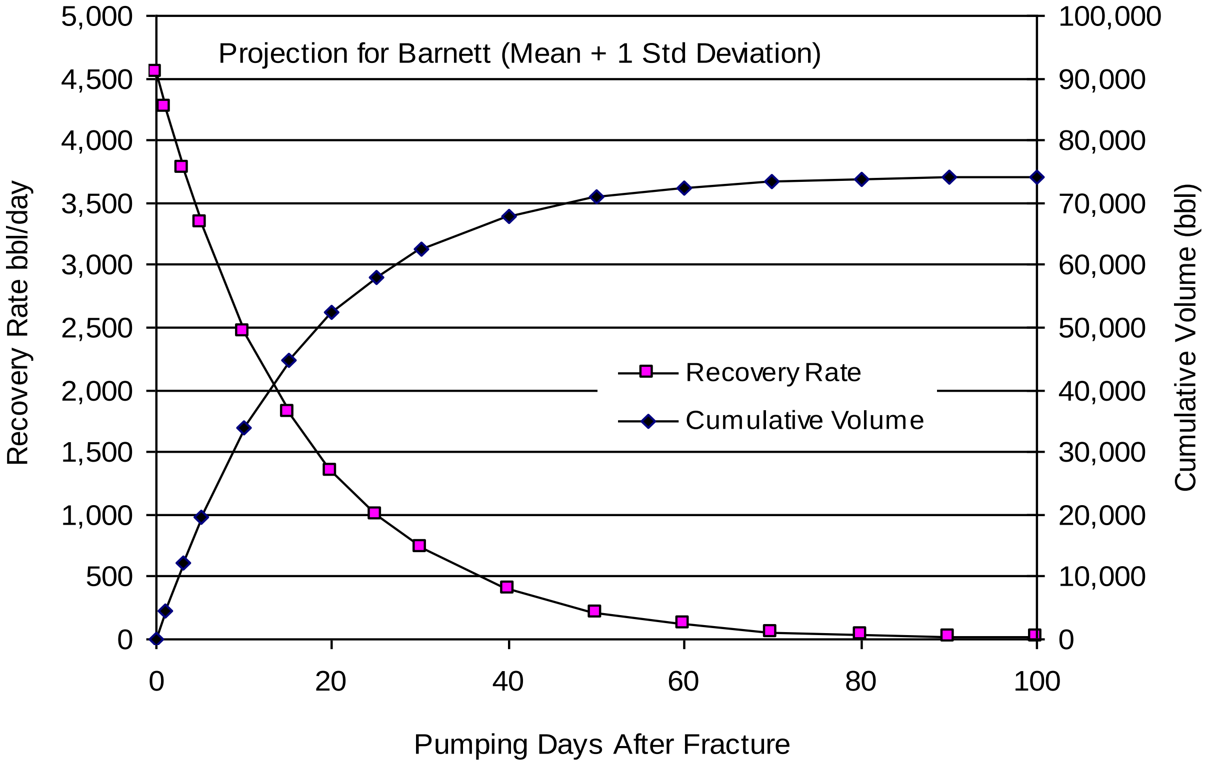

Figure 5-5: Projected Recovery Rate and Cumulative Volumes for the Mean (plus 1 standard deviation) Barnett Flowback Event as a function of Pump Days after Fracture.

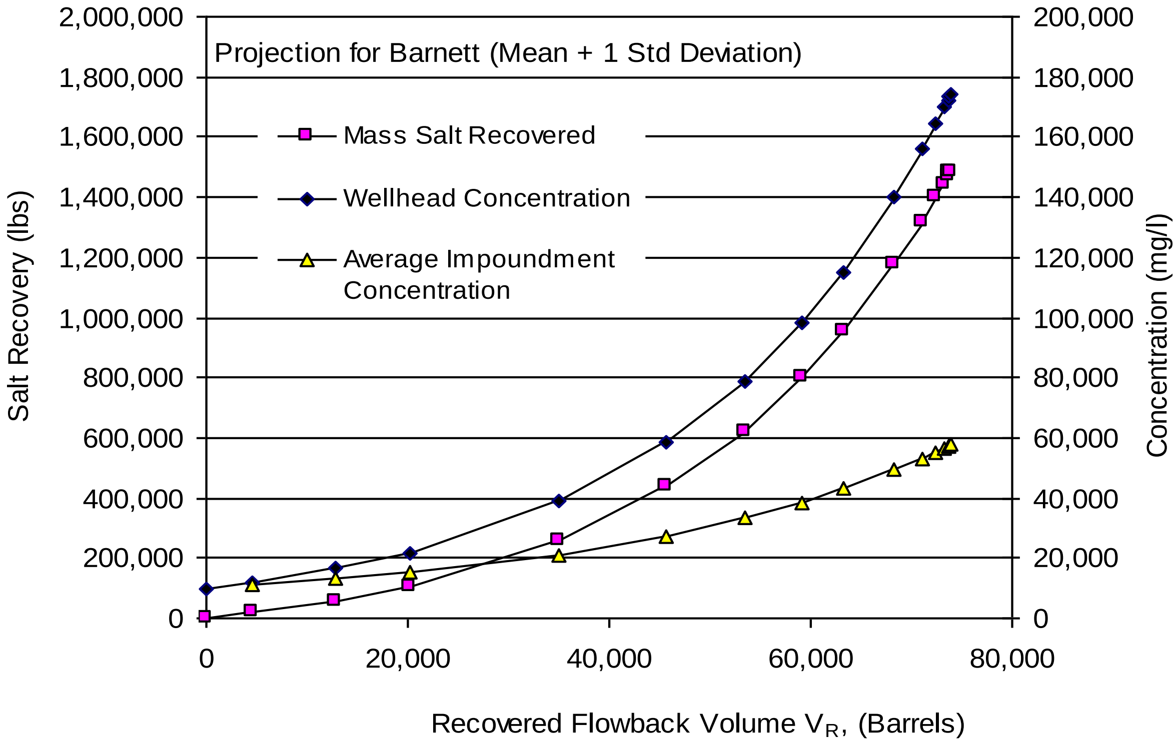

Figure 5-6: Projected Salt Mass, Wellhead Concentration, and Average Impoundment Concentration for the Mean Barnett Event (+1 Standard Deviation)

The empirical correlation between wellhead concentration and recovered flowback volume (Equation 5) is also not directly based on time. This is contrary to a dissolution mechanism, suggesting that additional salts do not dissolve into the shut-in water. Equation 5 is more reminiscent of an elution model, in which saturated ground water is initially flushed away from the well by the influx of relatively fresh fracture water. Recovery of the flowback water includes back-elution of the brine. In the initial data set for the Barnett (Galusky and Hayes, T,D., 2011) three sites were described that had were subjected to shut-in periods of up to 65 days. The analysis of these data with the present model (Severin et al. 2012b) indicated that the shut-in period did not influence the wellhead concentration. The data suggest that the concentration of flowback is more dependent on the total volume of recovered water than on the time of recovery. Recovery shutdown periods of up to 65 days had little bearing on the wellhead concentration.

Outlook The preliminary model suggested in this report points to several interesting differences between the Marcellus and the Barnett databases. Fractures in the Barnett region tend to show high initial salt concentrations and large initial fracture volumes, possibly due to water reuse practices within the region. The rate of flowback recovery in the Marcellus tends to occur more rapidly than in the Barnett. The empirical kinetic coefficients (k day^{-1}) in the Marcellus appear to be eight times greater than in the Barnett. A number of conjectures may be forwarded to explain this difference and include, perhaps, fundamental differences in the porosity of the fractured shale, differences in regional fracture technique, or differences in management style. The saturated background water concentration, C_S, appears to be higher in the Marcellus region than in the Barnett. This is likely a difference in the subsurface chemistries in the two regions. It may be further speculated that other geographic regions will also show important and interesting differences in the hydrofracture data.

Future Considerations Specific conductance can be readily measured, calibrated and automated. The close correlation between TDS and conductance indicates that operators should be able to measure, separate and segregate flowback waters in real time using in-line conductivity transducers more or less according to the scheme presented below in Figure 5-7. In simple terms, flowback water would be analyzed in real time using an electronic, recording electrical conductivity sensor. This would be coupled to an electronically operated valve that would shunt water to different storage facilities according to programmed levels of measured conductivity. The numeric criteria for determining number and levels of measured conductivity would be determined based upon operational needs and logistical constraints.

In the example shown in Figure 5-7, the lowest TDS waters would presumably be the most valuable to recover and recycle since these pose the least restraints and requirements with respect to handling, treatment and re-use. Yet, given the rapid rise in TDS it may not be realistic to capture nearly fresh (less than 3,000 TDS mg/kg) from Barnett shale gas flowback waters. However, if more realistic thresholds are set (say 10,000 mg/kg for low TDS waters and 25,000 mg/kg for high TDS waters) then such a system may afford realistic potential to recover and recycle early flowback waters and thus significantly reduce the total quantity of “new” water used to fracture subsequent wells.

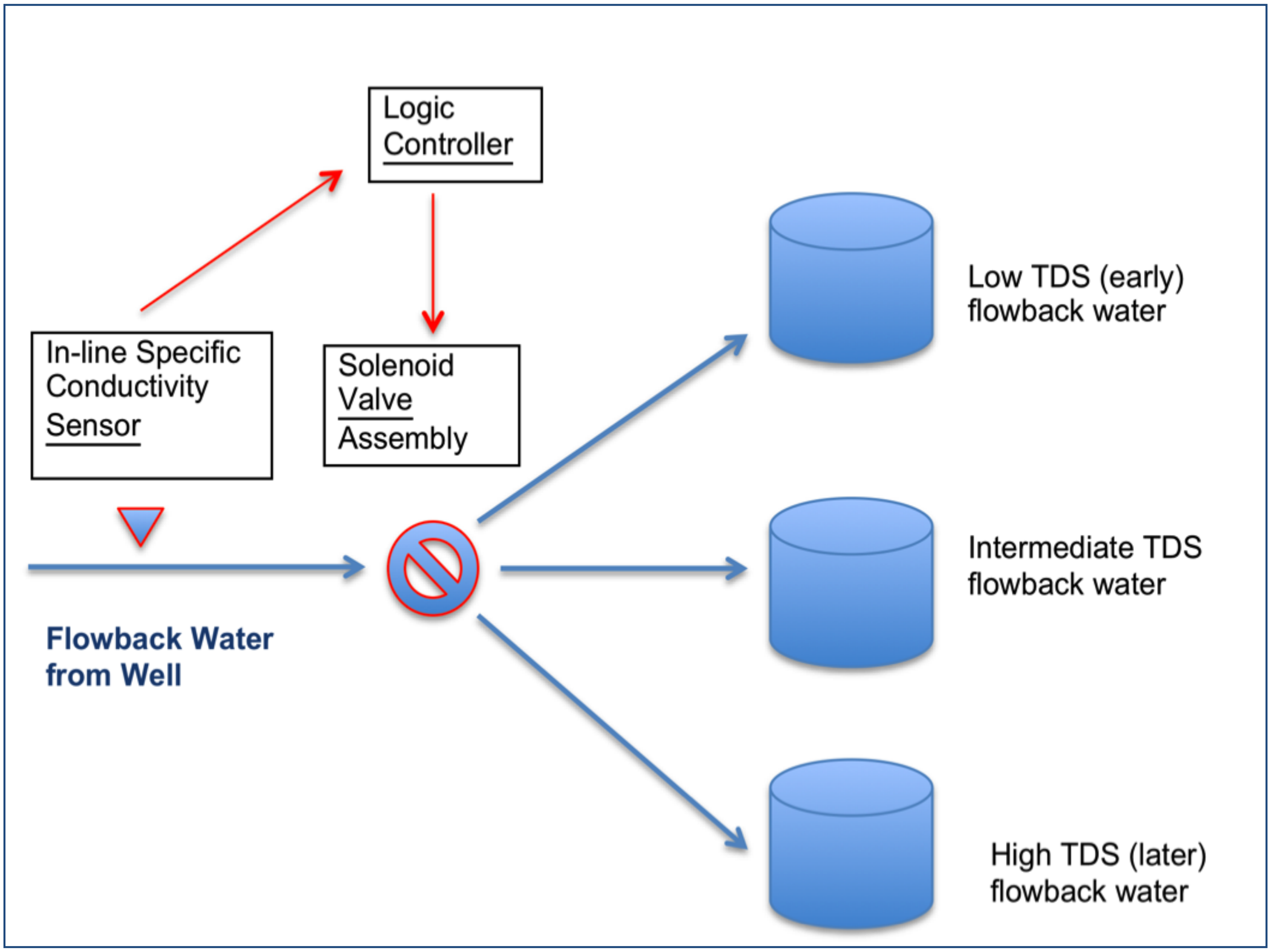

Figure 5-7: Hypothetical Flowback Measurement, Separation and Segregation System

Conclusions

Water management at hydraulic fracturing sites is becoming an important consideration in the economics and longevity of active wells. This paper presented a simplified hydraulic model based on the rate of flowback recovery as a function of recovered volume for 10 sites in the Barnett. Data suggested that recovery shut-down for the purposes of minimizing water recovery does not mitigate the flowback event. The simplified hydraulic model fit cumulative volume data from 13 sites in the Marcellus. The median projected recovered volume in the Barnett data set was several times greater per event, than in the Marcellus data set. The median kinetic coefficient for the Marcellus was eight times greater than for the Barnett. This suggests a different management strategy might be beneficial for the different geographic regions.

The preliminary model may be used as a tool for water reuse and water process selection. In the most rudimentary utility, the model may be used as a guide for segregation and isolation of relatively clean initial flowback water from heavy brine in late flowback waters. This selection tool may also be used to establish projections for the transportation costs, treatment process equipment, and treatment costs. The value of the modeling exercise is demonstrated as the basis for a broader life cycle analysis, as presented in another chapter of this report. (See Chapter 11: Systems Engineering and Life Cycle Analysis) and in a previously prepared topical report available from RPSEA (Hayes and Severin, 2012).

References

Hayes, T.D., (2009) Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas, Final Report to the Marcellus Shale Coalition. Gas Technology Institute, Des Plaines, IL.

Hayes, T.D. and B.F. Severin (February, 2012) Preliminary Engineering Systems Analysis of Shale Gas Water Management. RPSEA Report No. 08122-05.10.

6 Feasibility of Using Alternative Water Sources for Shale Gas Well Completions

Rationale

The study presented in this chapter investigates alternative sources of water to be used in the last completion phase (so-called “fracking”) of oil and gas wells in the Barnett Shale play. It focuses on more rural counties (Montague, Jack, Palo Pinto, Parker, Erath, Hood, Somervell, Bosque, and Hill) located to the west of the core area (Denton, Johnson, Tarrant, and Wise Counties). Millions of gallons are needed to perform the completion phase before oil and gas wells are put online, and, in the past years, operators have mostly used (1) groundwater from dedicated supply wells tapping the Trinity Aquifer, a major aquifer; (2) surface water from large reservoirs and rivers, purchasing it from water-rights owners (private or state agencies such as river authorities); and, to a lesser extent, (3) surface water from private ponds and other water bodies; (4) treated water from municipalities and industrial users; and (5) water recycled from previous fracking operations. As gas production moves away from the core area toward the north, south, and west where the Trinity aquifer is thin or absent to access the remainder of the play, Barnett Shale operators are faced with two challenges: (1) increased water scarcity and (2) measured reluctance to impact domestic and public water supplies. As a result, there is a need to assess the amount of water available and accessible to the industry.

Goals

The overall goal of the study is to quantify the amount of make-up water available from non-conventional sources (that is, not from large reservoirs, lakes, and rivers and major productive aquifers) in the footprint of the Barnett Shale, particularly outside of the core area. Recycling and treatment are not discussed in this chapter.

Objectives

The specific objectives of the study were to:

1. Gather baseline data and determine current and projected water use for fracking purposes,
2. Review water-quality specifications required to perform frac jobs developed by the Barnett Shale Water Conservation and Management Committee Frac Job Expert Panel,
3. Inventory alternate sources of water with the potential of meeting industry needs: (a) treated wastewater outfalls from waste water treatment plants; (b) small water bodies outside the State regulation of surface water, and (c) smallish groundwater aquifers in Paleozoic-age disconnected sand bodies west of the more plentiful Trinity aquifer.
4. Determine water compositions of alternate water sources by searching existing databases.
5. Determine technical and economic feasibility of utilizing alternate sources of water

Approach

Bullet (1) was accomplished through a synergetic parallel project funded by the State of Texas. Water use amounts were obtained from company records provided through a private vendor database. Water use projections for fracking were established by interacting with industry experts. Bullet (2) consisted in assessing the consistency of matter experts’ opinions (captured in a report and through discussions). The bulk of the work addressed bullets (3) and (4) and is described in more details below. Bullet (5) refers to the conclusion of this work.

Investigating the three main alternate water sources required the implementation of several distinctively unique approaches:

- Treated waste water amount and chemical quality was obtained by mining state (TCEQ) and federal databases (although not very straightforward).
- All non-State surface water bodies were inventoried through satellite orthoimagery coverage. They were sorted into six size categories (<0.25 acres to >50 acres) and computed for two selected years assumed to be representative of Texas climate cyclicity (“normal” wet and “normal” dry). The study assumes that the only water available from the surface water bodies is the balance between wet and dry conditions and that that volume is to be spent in the course of two years. Another important assumption applicable to smaller stock ponds is that they are filled up only through run-off and rainfall, not through groundwater pumping. Another concern was that the opportunity of selling water to the industry would incite landowners to create stock ponds filled with groundwater. This concern does not seem to bear out as comparison in water body count and total surface area between the reference years chosen as wet (1997) and dry (1999) (still early in the history of the Barnett play at which time gas production was restricted to the core area East of the zone of interest) and later years (2003 to 2010) shows no difference in water body coverage and count. Because depth of the surface water bodies is not well-know there is some uncertainty in the amount of water available. However, minimum and maximum depths as a function of water body size are relatively well known. A sampling of reservoirs present in the same area with known average depth was used to constrain water volume.
- Little is known about the Paleozoic aquifers in the footprint of the Barnett Shale (outside of the Trinity Aquifer). Although part of a larger hydrological system, most of them are small in size, barely covering a fraction of a county. Some are used for municipal water use (Montague County) but overall there is a need to determine what their capacity (how much water they hold), their yield (how much water can be produced from them), and water quality (fresh or brackish). Groundwater availability was inferred from the construction and running of a 4-layer numerical model of aquifers covering pre-Trinity Paleozoic formations present in the subsurface of the area of study. The development of the model was done following informal guidelines set by the state of Texas Groundwater Availability Model (GAM) program and entailed (1) development of a conceptual model that consists of a shallow flow system quickly discharging baseflow water to the streams with a general head gradient to the north; (2) a thorough and lengthy phase of data gathering (top and bottom of layers, hydraulic conductivity values) from the literature and from public-domain databases; and (3) a calibration phase of matching modeled heads to observed heads. The amount of water available for pumping was computed by taking into account projected water use from all other users and assuming that an average cumulative drawdown of 5 feet across the entire study area in the next 50 years was acceptable to all stakeholders. This value is consistent with values accepted in the State for other small aquifers. With the help of the aquifer numerical model, we were able to determine the level of pumping that would generate such an average drawdown. Although aquifers do contain immense amounts of water, the amount that can be withdrawn is quickly limited by negative environmental and other impacts consequences (drying of springs, no base flow, disappearance of phreatophytes, subsidence, necessary lowering of pumps, etc).

BEG's team developed an Arc-GIS tool to determine the amount of water available at any point of the study area from the three characterized water sources within a given radius, chosen at 5, 10, and 15 miles. To understand the adequacy of the resource, ~1000 points were selected on a regular grid (Δx= 4406 m and Δy=4530 m) covering the area of interest and statistics on water availability were then derived. Points are numerous enough to be representative of any point in the area of interest. The tool could be used at any given point outside of the chosen set and is accurate for treatment plants, somewhat less accurate for surface water bodies (because of the uncertainty on depth), and the uncertainty is higher for groundwater use because the model is regional in nature (that is, acceptable in its general behavior but not necessarily accurate at the local scale). Although the three categories have their own units of convenience, we need to express them under a unique system in order to compare them. Several approaches can be devised to reach such objective. The approach chosen in this work is to notice that operators store most of the needed frac water on site in the few weeks leading to the fracking of the well. We assumed that that lead time is one month (1/12th of a year). Treatment plant data is expressed as a rate and represents an annual average expressed as an average daily rate. We assume such water source is available year-round. Surface water body reference characteristic is volume. However, not all of the water is necessarily available. The primary purpose of the ponds / water bodies is irrigation, cattle, and for the smallest stock ponds fish farming. We assume that the true water available is the volume difference between wet and dry years. How much can be withdrawn from them in a short period of time is more related to pump power. Another, maybe more relevant, factor is how fast the ponds can be replenished. Making the assumption that Texas weather oscillates between "normal" dry and "normal" wet years on average, this volume of water can be used up over a period of 24 months. Pumping from aquifers is determined by the model and assumed constant through time.

Results and Discussions

Current and projected water use by county is documented in a report in the public domain (http://www.twdb.state.tx.us/RWPG/rpgm_rpts/0904830939_MiningWaterUse.pdf). The amount of water used across the play is variable from one year to the next but is in the tens of thousands of acre-feet (AF) per year (~25,000 AF in 2008) corresponding to thousands of wells being fracked (~2500 in 2008). The amount of water used per unit length of lateral is approximately 1000 gal/ft. The split between surface water and groundwater is unknown but thought to be relatively even. The industry has made significant progress in the behavior of additives since the initial expert meeting in 2008. The additives can now handle brackish water (<10,000 mg/L) without problem.

BEG now discusses the three alternate water sources. There are approximately 160 waste water treatment plants in the area of study, 5 of them are very large (>100 million gallons per day -MGD) and not included in the study. Most of them are small to very small. Not considering the large plants, average outfall flow is 0.689 MGD but median is much lower at 0.087 MGD. Percentiles are as follow: 95th = 4.3 MGD, 75th = 0.37 MGD, 50th = 0.087 MGD, 25th = 0.01; 5th = 0.002; minimum <0.001 MGD. Those rates and chemical quality of treated waste water (< 1000 mg/L) are fairly constant throughout the year. Numerous water bodies are present and represent a substantial amount of water even without including large lakes. Overall there was ~31,200 and ~12,400 small water bodies totaling ~51,000 and 23,500 acres in wet and dry conditions of the selected years, respectively. The corresponding water volume are then approximately 0.54 million acre-feet (AF) in wet conditions and 0.2 million AF in dry conditions, again not including large reservoirs. The surface water quality is understood to be fresh.

Paleozoic aquifers are sometimes the only water source in large sections of the Barnett Shale footprint, with no surface water bodies and no water treatment plant in those sparsely populated areas. Those aquifers provide fresh to brackish water from generally low-yield wells. An evaluation of water well characteristics in our 2,474-well database reveals median values for depth of 200 feet, discharge rate of 11 gallons per minute, and screen length of 35 feet. The fact that the state of Texas has never catalogued North-Central Texas Paleozoic aquifers even as minor aquifers strongly suggests that they can only provide small amounts of water. This, in turn, suggests that obtaining meaningful amounts of water will require long and deep screened intervals tapping into more brackish sections and producing a degraded water quality. Groundwater total dissolved solids are generally potable <300 feet, but increase rapidly down dip. The modeling suggests that approximately 15 MGD of groundwater is available across the area.

Treatment plant outfall, surface water bodies, and aquifers represent vastly different water source types. Considering a unifying concept helps in characterizing them. We used two parameters: capacity of storage and yield. The former addresses how much water is available at a given time, the latter informs on how fast the water can be accessed. Treatment plant outfalls have no capacity but sustained known yield. If the water is not used immediately it is discharged into streams or lakes, becomes water of the state, and is lost for the purpose of this work. Aquifers have a large storage capacity but delivery of the water is constrained by the maximum well yield and the ability of the aquifer to recover. Surface water bodies are relatively numerous and widespread across the area of interest but most of them are small with limited capacity even few large bodies exist. The following summarizes these qualifiers across example categories: 1) Treatment plants: no capacity, possibly large yield; 2) Surface water bodies: large capacity, medium to large yield; and 3) Aquifers: medium capacity, small yield. A third qualifier (distance) can be added and considered. Treatment plants exist only at very well-defined locations and are not that common whereas aquifers are ubiquitous even if not necessarily productive at every location. Surface water bodies are relatively common but mostly small.

Not surprisingly the amount of water available increases as the search radius increases. For treatment plants, from none (in most cases) or less than 5 million gallons per month (8-km radios case) to none (~30% of cases) to less than 15 million gallons per month in the 16-km radius case to none (in ~15% of cases) to a solid 5 to 10 million gallons per month and a large spread all the way to 180 million gallons per month in the 24-km radius case. Surface water is generally available (except at 10 to 15% of the locations) with a large spread and no clear mode to 150, 400, and 800 million gallons per month in the 8-, 16-, and 24-km radius case, respectively. Groundwater is not available from wells with sufficient yield at 50%, 33%, and 21% of the locations in the 8-, 16-, and 24-km radius case, respectively. When it is available amount ranges from a few million gallons per month to ~30, ~80, and ~150 million gallon per month in the 8-, 16-, and 24-km radius case, respectively. The combined amount displays a clear mode at ~35 million gallons per month with a long tail to ~150 million gallons per month in the 8-km radius case but is more uniformly distributed in the 16- and 24-km radius case ranging from almost nothing to 500 and 950 million gallons per month, respectively. Detailed results are presented in the deliverables itemized below.

Results indicate that, assuming a dense development of the oil and gas resource, in most cases enough water is theoretically available on average (~40 million gallons available vs. ~10 million gallons used per month in a 5-mile radius). However, more than half of the total is surface water making it very susceptible to droughts. Droughts will do more than drying up the surface water resource, it will also limit access to treated waste water and groundwater as conservation takes place and as more users rely on groundwater, respectively. From an economic standpoint, all the alternative sources described in the study are very fragmented leading to a diffuse ownership and likely expensive water gathering system.

Deliverables

Topical Reports

Nicot,J-P., and Hayes, T.D. (2010) Feasibility of Using Alternative Water Sources for Shale Gas Well Completions —A Preliminary Guidance Document on Current Practices in the Barnett, Report No. 08122-05.01, Barnett and Appalachian Shale Water Management and Reuse Technologies, RPSEA Contract 08122-05.

Nicot,J-P., Wolaver B.D, Huang, Y.,Howard, T., Costley, R.A., Breton ,C., Walden S., Baier R., Strassberg G., McGlynn E., Hingst M., Mercier J., Lam, C. and Hayes, T.D. (2012) Feasibility of Using Alternative Water Sources for Shale Gas Well Completions — Final Report, Report No. 08122-05.02, Barnett and Appalachian Shale Water Management and Reuse Technologies, RPSEA Contract 08122-05.

Impact to Producers

The main result of the study is that water is present in quantities sufficient to cover fracking needs but is unequally spatially distributed, prone to droughts, and very fragmented. Producers who are willing to consider expenditures that reduce uncertainties of water availability would be better off relying on more distant but more abundant water sources.

Conclusions and Recommendations

A summary of the water availability distribution in the rural-county area-of-interest of the Barnett Shale is shown in Table 6-1. This table suggests that, in 50% of cases, at least 42.7 million gallons will be available per month in any 5-mile radius. To put the matter in perspective, assuming a spacing between laterals of 1,000 feet, an average water intensity of 1000 gal/foot, and a maximum coverage of laterals for gas production yields $5280 \times 5280\ ft^2 / 1000\ ft \times 1000$ gal/ft, that is, a maximum water use of 27.9 million gallons per square mile or 2190 million gallons to be distributed through time. Assuming an active life of 20 years of fracking in a given development area, this level of water use amounts to a water use of 9.1 million gallons per month, or 21% of the median of water availability.

Taking the analysis further, in “normal conditions” with wet and dry cycles the amount of water seems adequate, however it is very dispersed and distributed spatially, at the exception of a few larger waste water treatment plants. In addition, surface water does represent a significant fraction of the available water. In times of sustained drought (>2 years), there is no surface water available and the groundwater resource is somewhat reduced as all users relying on surface water will fall back on groundwater. Waste water treatment plant outfall availability will also be reduced because water conservation will be emphasized and because cities and towns may preempt the use of the treated water.

Table 6-1: Summary of Results: Water Availability Distribution

Table 6-1 also suggests that a drought scenario will prevent operators from using local water. The median for the 5-mile radius case shows that only surface water is a plausible source of water, though it will not be available during a drought. Operators would have to go further out from the well location to access the needed water. The median available water for the 10 mile case is 223 million gallon per month of which ~80% is surface water not accessible in time of drought, the remainder of about 30 million gallons consists of approximately 60% groundwater and 40% treatment plant outfall (note that the median of the sum is not necessarily the sum of the medians). Because all of it will not be accessible, the amount of water theoretically available becomes very close to the amount required by operators.

What is missing from this document is a detailed economic analysis, the discussion above does not include the possibility that not all the water is actually accessible to operators because of land ownership or other factors. The extreme fragmentation of the resource also suggests a pipeline gathering system greater than 60 miles per well or equivalently trucking the water from many different places, many undoubtedly without easy road access.

Table 6-1: Summary of Results: Water Availability Distribution

	Treatment Plant (Mgal/ month)	Surface Water (Mgal/ month)	Ground-water (Mgal/ month)	Combined (Mgal/ month)	Average Weighted Distance (miles)	Ground-water Discharge Median (gpm)	Ground-water Discharge 95th Percen. (gpm)	Transmis-sivity Median (ft^2/day)	Transmis-sivity 95th Percen. (ft^2/day)
5 miles (8 km) radius									
5th Percen.	0.0	0.0	0.0	5.2	2.7	8.8	14.8	3.3	35.2
Median	0.0	35.9	0.0	42.7	3.3	27.6	33.4	301	767
95th Percen.	45.6	98.3	22.6	118	4.0	42.6	49.4	1675	3799
10 miles (16 km) radius									
5th Percen.	0.0	0.0	0.0	33.6	5.7	9.4	18.6	4.6	158
Median	7.1	183	8.9	223	6.6	27.5	36.2	316	1239
95th Percen.	117.1	358	70.6	447	7.6	39.4	49.6	1195	3859
15 miles (24 km) radius									
5th Percen.	0.0	0.0	0.0	79.4	8.8	10.0	21.2	5.7	297
Median	44.7	382	31.5	462	10.0	27.4	37.8	316	1750
95th Percen.	167.7	682	121	838	11.1	37.2	52.5	744	3315

Future Considerations

Overall, in normal conditions, operators should find enough water from surface water bodies complemented by groundwater and possibly waste water treatment plant outfall to sustain . The major issue is the extreme fragmentation of the resource among many small water bodies, low-yield water wells, and some waste water streams, generating a collection cost that may not be overcome in the less productive areas of the play. In addition, drought conditions will seriously handicap production of these western counties of the Barnett play unless water is brought in from far away from either conventional or possibly alternative resources.

7 Engineering Decision Tool for the Evaluation of Mechanical Vapor Recompression for the Treatment of Shale Gas Flowback Water

Rationale

Long-term water management in the shale gas industry will depend heavily on maximizing water reuse while minimizing disposal volume. Certain treatment processes, such as mechanical vapor recompression (MVR), will be employed by the industry to meet these needs. MVR is an energy efficient distillation process that provides a large volume of (nearly) deionized water and a small volume of highly concentrated brine. This task was undertaken to provide an engineering analysis of a full scale pre-treatment and MVR plant actively treating 6,000–6,800 barrels per day of flowback water in the Barnett. Chemical data, energy utilization, and economic data are provided.

Objectives

The purpose of this project was to document the field performance of the NOMAD MVR system in the demineralization of shale gas waters in a near-field brine processing facility owned by Devon Energy and operated by Fountain Quail. Performance characterization included determination of mass flows, energy flows, fate of constituents of interest, product water yield and product water quality. This report has been prepared by GTI to provide managers and engineers with a technical information base for decision making regarding the value and potential role of the MVR process in the long range management of brines and salts throughout the water-based life cycle of each shale gas development area.

Goals

Testing under real world conditions allowed the determination of actual field conditions (including feed water quality) on the stability and performance of the entire MVR system, including pretreatment and thermal skid units. Test plan development, coordination and data compilation and analysis were all coordinated by the Gas Technology Institute to provide a third party assessment of the MVR system in the demineralization of a blend of flowback and produced water from shale gas well fields in the Barnett.

Approach

Mechanical vapor recompression is a highly efficient distillation process. A mechanically-driven blower or compressor is used to increase the pressure of the vapor that is produced from the boiler in order to improve heat transfer efficiencies. An increase in the water vapor pressure increases the condensation temperature of the steam rendering it useable for heating the original mixture (in the boiler) in a heat transfer device or heat exchanger. The major advantage of mechanical recompression over conventional distillation is the ability to recycle the latent heat of flashed vapors to the bottom fluids, saving 10-15 % of the total energy of distillation.

Mechanical vapor recompression has become a standard method of distillation since its commercial introduction in the 1960's. The process has been employed at thousands of facilities for the desalination of sea water (Veil, 2008), the crystallization of sugars in the food industry, dewatering of products in the chemicals and pharmaceuticals industries (Becker and Zakak, 1985), and more lately, in the recovery of industrial wastewaters.

Veil (2008) presented a cursory evaluation of the Aqua Pure MVRs at the Devon Energy water reclamation facility in Decatur, Texas. This site (also called the "Maggie Spain Facility" which is the subject of the present report) treats flowback water and process water from Devon's shale gas wells located at multiple well fields in Denton County.

This report provides a detailed description of the Maggie Spain process train and its performance during a 2-month period. Water chemistry samples and measurements were taken to characterize mass and energy flows throughout the entire treatment system.

Results and Discussion

Maggie Spain Facility: The Maggie Spain Facility (Figure 7-1) is comprised of an influent impoundment and a water preconditioning train followed by multiple mechanical vapor recompression (MVR) modules. The MVR's are operated in parallel to generate a demineralized product water stream and a concentrate stream. The diluate, representing >70% of the water flow is discharged to a product water impoundment. The concentrate, representing less than 30% of the water flow and greater than 99% of the TDS is collected in effluent storage tanks for future disposal. Figure 7-1 shows the locations in the flowsheet where water samples were taken for analysis (sampling twice weekly). Analyses included conductance, total organic carbon, BTEX (benzene, toluene, ethyl benzene, and xylenes), TPH (total petroleum hydrocarbons), total heavy metals, total dissolved solids (TDS), suspended solids, pH, alkalinity, sulfate, total ammonia, and phosphorus.

All of the energy required by the facility is supplied by natural gas that is provided by the shale gas wells of Devon Energy. The electricity required for pretreatment, and general site needs is supplied by two natural gas driven generators. Each NOMAD MVR skid is powered by an internal combustion engine fueled by natural gas (each engine capable of delivering up to 700 hp). Total energy demand measurements were obtained from daily readings of the natural gas utilization at the facility.

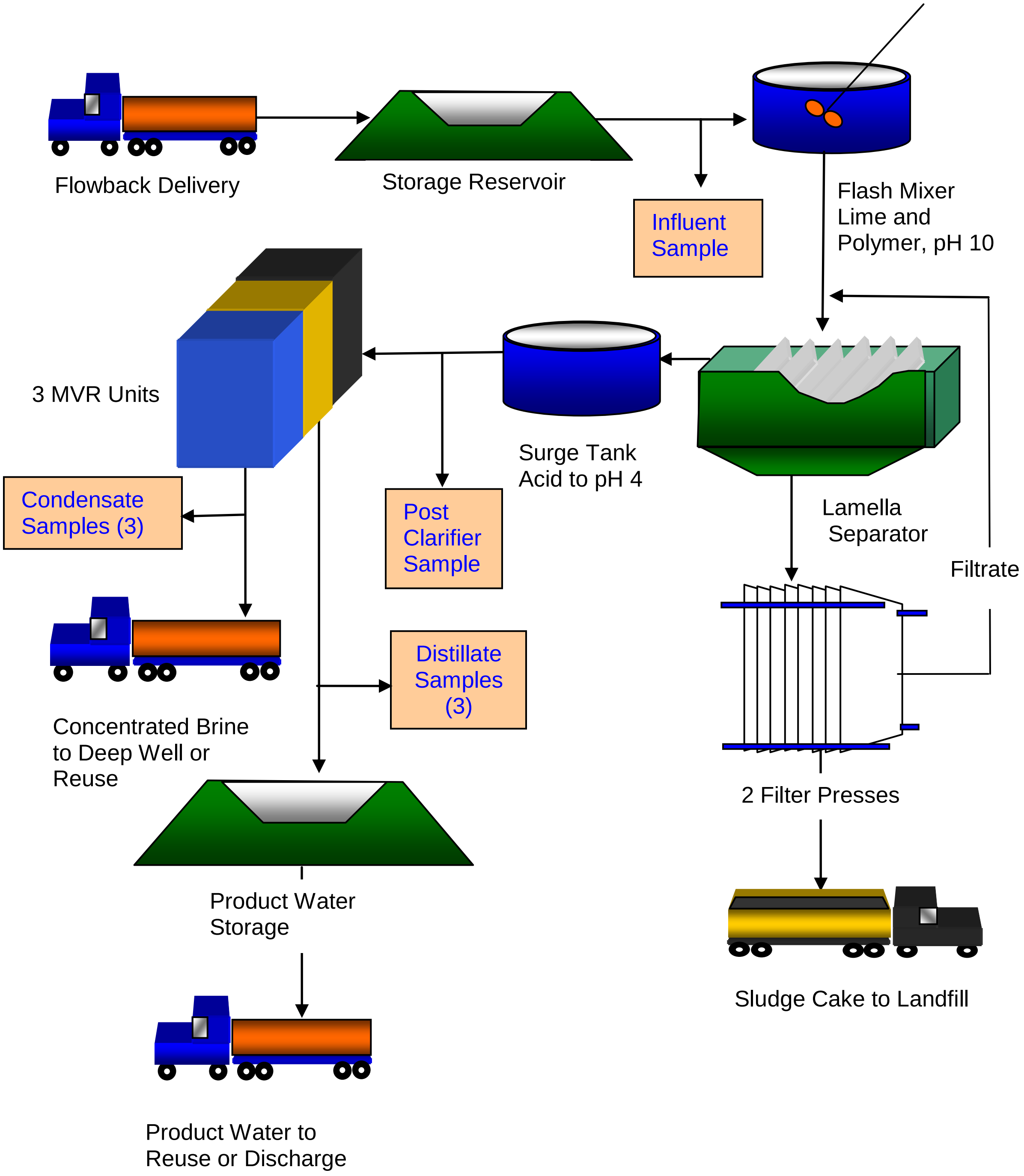

Figure 7-1: MVR Process Flow Sheet, Maggie Spain Facility

***Preconditioning**:* The preconditioning section of the Maggie Spain facility provides suspended solids removal, oil & grease control, iron removal, and calcium-stable water. Water is delivered daily by truck at a rate of 4,000 to 6,000 bbl/d to a 1.4 acre storage reservoir. The chemical analysis of the water leaving the reservoir, (representing influent water to the clarifier) is presented in Table 7-1. The average total dissolved solids are about 50,000 mg/l. The raw water contains a number of scale forming cations, including calcium, iron, strontium, magnesium and barium. Small amounts of total petroleum hydrocarbons and BTEX are also present.

Table 7-1: Influent and Post Clarifier Water Analysis

All units are in mg/l except pH and Conductance (mS/cm)	Influent Water			Post Clarifier		
	Average	Median	Standard Deviation	Average	Median	Standard Deviation
Specific Conductance	55,835	55,650	24,890	57,989	61,050	24,243
Total Dissolved Solids	49,550	44,900	10,959	49,133	46,900	9,921
Total Suspended Solids	1,272	357	3,443	140	132	45
pH	NA	6.9	6.7 - 7.7	NA	3.7	3.1 - 4.6
Alkalinity	405	385	126	12	4	14
Total Organic Carbon	42	12	118	10	9	5
TPH*	388*	19	1,363	5	4	2
BTEX	3.3	2.9	1.4	2.3	2.1	0.8
Ammonia	84	84	26	81	84	24
Sulfate	309	316	153	221	205	123
Phosphorus	3	3	2	2	2	1
Barium	15	7	19	13	6	17
Boron	17	18	4	16	16	3
alcium	2,916	2,570	975	2,876	2,705	922
Iron	28	27	10	3	2	3
Lithium	12	11	3	12	11	3
Magnesium	316	291	131	319	296	114
Potassium	484	296	524	504	349	494
Sodium	10,741	10,700	3,622	12,400	12,100	2,821
Strontium	505	467	182	528	483	161
Note(*) TPH data overwhelmed by a single event of 5,893 mg/l. The TPH average is 38 ± 43 when this event is disregarded.						

Water from the storage reservoir is sent to a clarifying process unit containing a flash-mix chamber and a lamella clarifier (Photo 7-1). Caustic (NaOH) is added at the flash mixer 1 to increase in the pH of the water to about pH10. The shift in pH causes much of the iron to precipitate. Polymer is occasionally added to aide in the coagulation of the solids.

Precipitated iron and other suspended solids are removed across a lamella plate clarifier (Photo 7-2). The clarifier removes about 90% of the suspended solids, including 90% of the influent iron. The chemical analysis of the post clarifier water is presented in Table 7-1.

The solids from the clarifier are dewatered with a pair plate and frame filter presses (Photo 7-3). The solids contribution from the clarifiers to the filter is about 2,500 dry pounds per day.

The cake solids produced from the presses are about 20-25% dry matter, yielding a wetted solids stream of 10,000 to 12,500 pounds wet solids per day. A 20 yard tote is removed from the site about once per week. The solids are sent to a landfill.

Clarified water is sent to a surge tank where the pH is adjusted to pH 4 to stabilize the scale forming cations, such as calcium. The pH adjusted water is the feed to the MVR units.

Photo 7-1: Flash Mixer and Clarifier
Photo 7-2: Details of the Lamella
Photo 7-3: Filter Presses & Tote

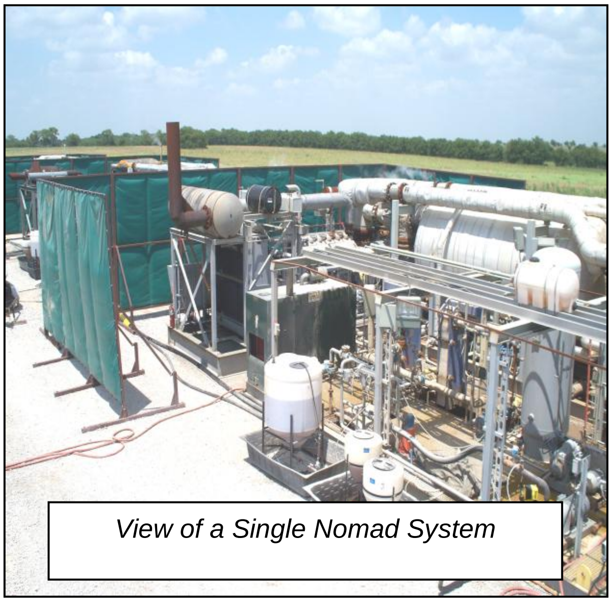
View of a Single Nomad System

Photo 7-4: NOMAD Skid Unit

Mechanical Vapor Recompression:

Mechanical vapor recompression (MVR) process is viewed by a number of shale gas companies as one of the most reliable methods of recovering demineralized water from concentrated brines. For this reason, Devon Energy has supported the demonstration of three modular NOMAD units that are manufactured by Aqua-Pure Ventures and operated in the field by Fountain Quail Water Management. The Maggie Spain facility has three mechanical vapor recompression modules (Aqua Pure NOMAD systems). These units are powered by natural gas, including the boiler that is used to bring the module up to temperature during startup and the 700 hp natural-gas-fueled internal combustion engine that drives the compressor. Electricity used for ancillary lighting, controls and data acquisition is supplied by one of the on-site generators. The footprint of the NOMAD facility is modest; a three NOMAD processing facility occupies an area of about 250’ x 250’ (about 1.4 acres). Each module (Photo 7-4) has a processing capacity of up to 2,800 bbl/d of influent brine.


Photo 7-5: Compressor Engine Skid

Each Aqua Pure NOMAD system consists of chemical conditioning plus three skids; 1) Pretreatment 2) Engine and, 3) Evaporator Heat Exchanger Skids. Chemical conditioning consists of anti-foam agents and corrosion control. The pretreatment skid provides 5μ bag filtration and pre-heating economizers. The engine skid (Photo 7-5) houses a mechanical compressor driven by an internal combustion engine that is operated on natural gas. The evaporator skid (Photo 7-6) provides the liquid-vapor heat exchangers, evaporator tank, and distillate collection tank.


Photo 7-6: Evaporator Skid

The process (Figure 7-2) is initiated by heating a portion of water from the distillate collection tank with an auxiliary start-up boiler. When the process comes-up to temperature, the boiler is extinguished.

The mechanical compressor (Photo 7-5) is fed a balanced mixture of vapor (fresh distillate) from the vapor separating concentrate tank and water (existing distillate) from the distillate collection tank. The compressor increases the fluid pressure creating a saturated vapor.

The saturated vapor enters a liquid/vapor heat exchanger on the exchanger skid (Photo 7-6). The hot side of the exchanger is the saturated distillate vapor. The cool side of the exchanger is concentrated liquor fed from the vapor separating concentrate tank. The process is designed to vaporize about 10% of the concentrate liquor.

The overall water balance for typical operation was generated by examining distribution of water between the distillate and concentrate of the individual MVR units (Table 7-2). Figure 7-3 is a plot of distillate and concentrate volume versus the volume fed to each unit. The slope of each line represents the fraction of the influent recovered. The MVRs, as operated in this process period, generated 72.5% distillate and 27.5% concentrate.

The overall salt balance for typical operation was generated by examining the distribution of TDS between the distillate and concentrate of the individual MVR's. This evaluation is presented in Figure 7-4. The slope of each line represents the fraction recovered in that process stream. The plot shows that the concentrate reliably contains >99.7% of the total salts while less than 0.3% remains in the distillate.

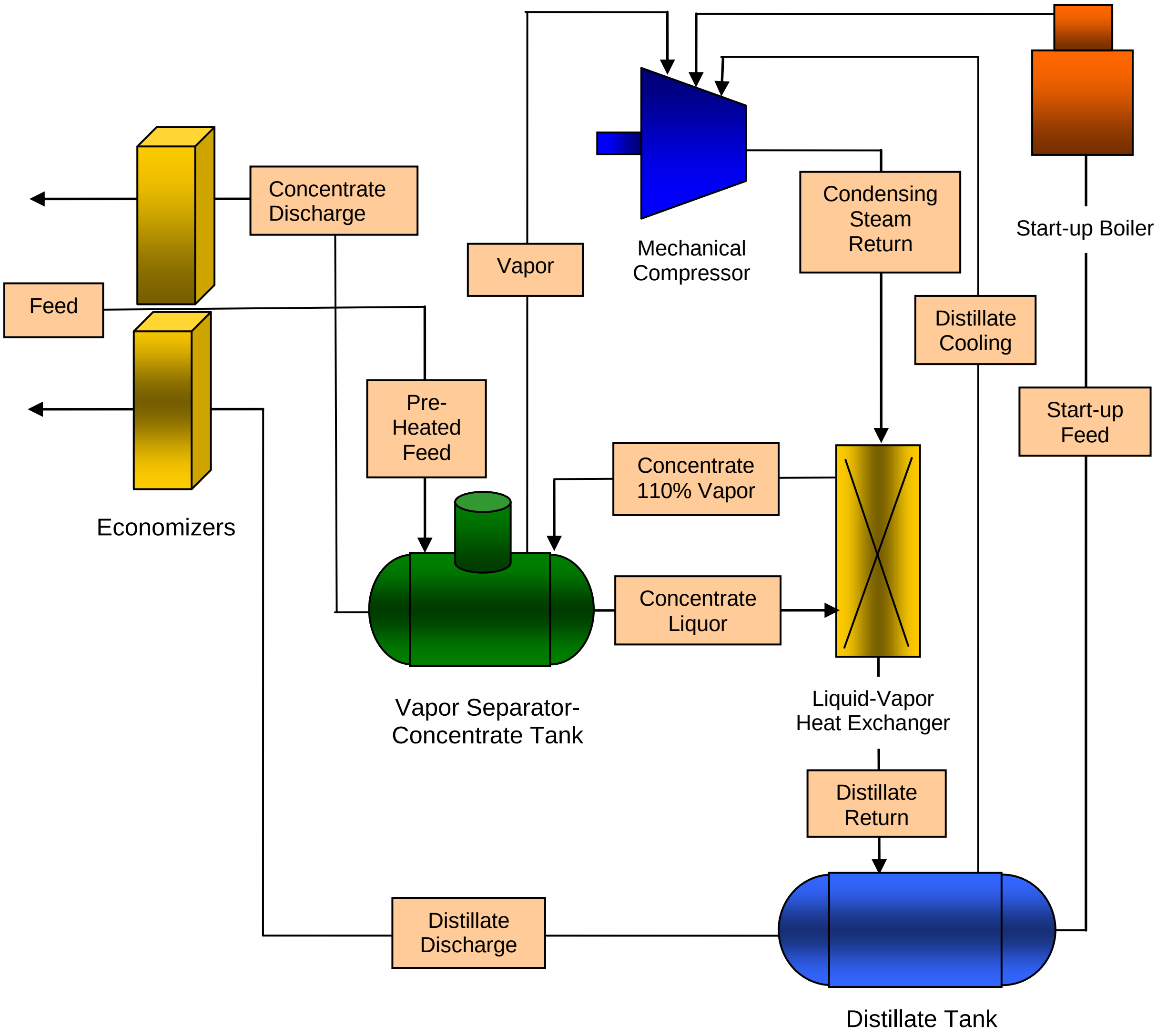

Figure 7-2: Simplified Flow Diagram for the Aqua Pure Mechanical Vapor Recompression Process

Total daily natural gas consumption (SCFD) was measured for the entire Maggie Spain facility. Energy consumption for individual Nomad MVRs was unavailable. Total natural gas demand was plotted as a function of overall influent loading and product water yield to determine the overall energy requirement for the facility (including MVR operation plus electricity generation). Figure 7-5 is a graph of total SCF gas utilization as a function of treated water or distillate generated. The plots appear linear with respect to either total volume of water treated, or the volume of distillate produced. The slopes of the lines in this plot indicate that the process requires about 48 SCF/bbl influent or 60.5 SCF/bbl distillate produced above the base loading.

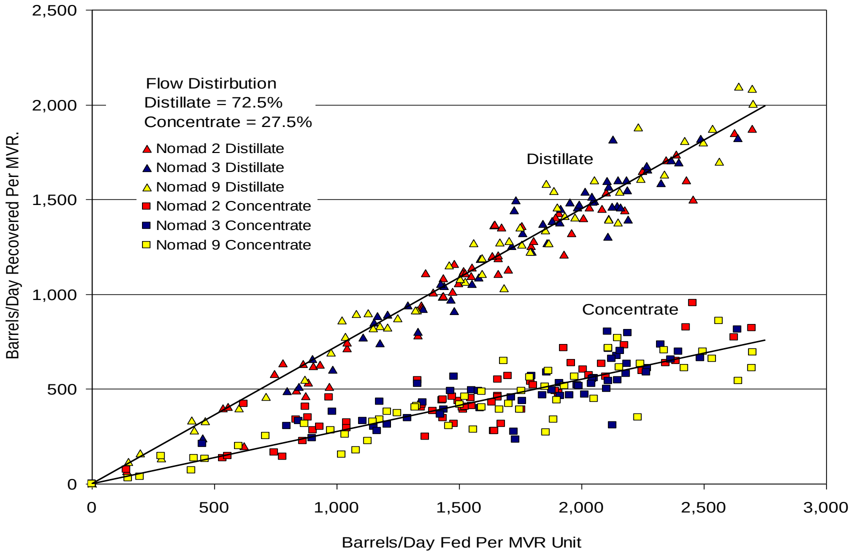

Figure 7-3: Water Distribution between Distillate and Concentrate During 60 Day Sample Period

Table 7-2: Chemical Analysis of the Distillate and Concentrate Streams Combined Data from Three MVR's

All units (mg/l) except pH And Conductance (mS/cm)	Nomad MVR Distillate*			Nomad MVR Concentrate		
	Average	Median	Standard Dev	Average	Median	Standard Dev
Specific Conductance	267	161	280	162,818	158,500	83,327
Total Dissolved Solids	171	103	179	168,465	162,000	29,239
Total Suspended Solids	9	4	12	617	519	319
pH	NA	10.7	10.5-10.9	NA	6.7	6.3-6.8
Alkalinity	263	248	85	162	143	73
Total Organic Carbon	22	16	17	12	12	4
TPH	4.6	4.0	2.3	4.3	4.0	1.1
BTEX	0.2	0.1	0.2	0.0	0.0	0.0
Ammonia	68	64	26	113	114	50
Sulfate	6	5	2	887	793	631
Phosphorus	0.1	0.1	0.2	7	6	8
Barium	0.1	0.1	0.0	27	5	48
Boron	0.4	0.4	0.1	63	62	13
Calcium	3.2	0.8	6.8	9,699	8,960	2,485
Iron	0.1	0.1	0.0	4	2	4
Lithium	0.1	0.1	0.0	42	38	11
Magnesium	0.4	0.1	0.8	1,132	1,055	355
Potassium	0.5	0.1	1.4	2,028	1,675	1,576
Sodium	14.3	3.6	31.6	41,302	39,000	8,046
Strontium	0.5	0.1	1.0	1,739	1,735	430
*Distillate TDS calculated from specific conductance						

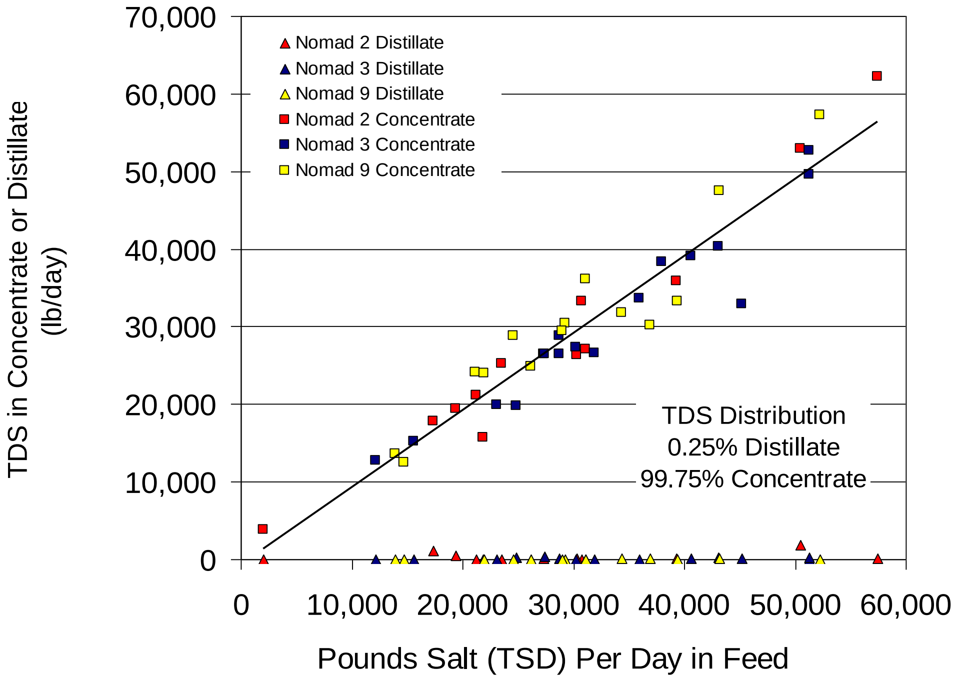

Figure 7-4: Distribution of Dissolved Salts between the Distillate and the Condensate Streams During 60 Day Sample Period

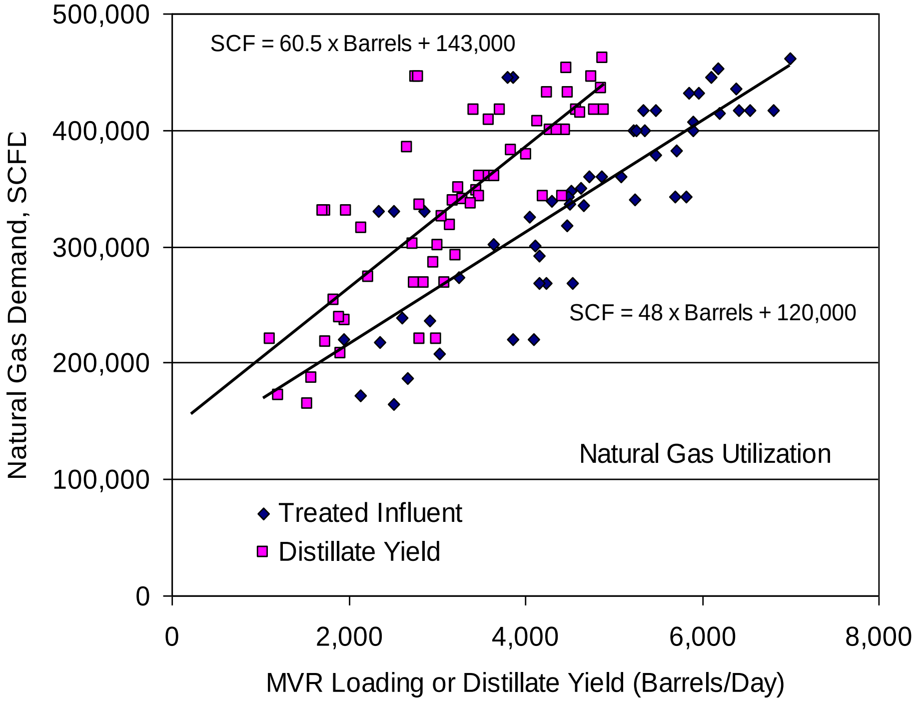

Figure 7-5: Daily Natural Gas Demand Versus Influent Loading and Distillate Product Yield
(Composite of Three MVR Units

Some of the scatter in the data is inevitably due to other process loads on the generators, such as drive motors and hydraulic pumps on the clarifier and filter press skids, site lighting, and miscellaneous office and maintenance activities. The raw gas numbers also include inefficiencies in electricity generation and transmission. Assuming that the field efficiency of the gas generators is about 35% to produce the required electricity, then the value of 60.5 SCF/bbl distillate is equivalent to 6.4 kWh/bbl distillate. This is convincingly within the range of results reported for electrically driven MVR's (Letterman, 1983; Gallarani et. al., 2002). If the apparent base load is added to the incremental processing energy requirements, the overall treatment requires 72 SFC per barrel treated, or 100 SCF per barrel distillate produced.

Fate of Various Chemical Constituents

Suspended solids removal occurs at the clarifier with about 90% removal by settling. The remaining suspended solids are removed to the concentrate stream. It is also possible that certain cations, such as barium and strontium, reach saturation equilibrium within the MVR concentrate stream and generate excess suspended material.

The fate total petroleum hydrocarbons (TPH) is apparently intimiately tied to the initial suspended solids. More than 84% is removed by clarification, and presumably is removed with the sludge cake from the filter press. Note that TPH data are overwhelmed by a single event of 5,893 mg/l. The TPH average is 38 ± 43 when this event is disregarded.

Total BTEX (benzene, toluene, ethylbenzene, and xylene) represents a volatile fraction of the organic matter in the water stream (Figure 7-6). Some (30%) of the BTEX is removed between the influent and the end of the clarification process.

Presumably, much of this removal occurs at the rapid mix tank from suface volatility. Much of the remaining BTEX is removed (additional 90-95%) in the MRV process. It is likely that these organic components are volatilized and expelled at degassing or pressure relief valves throughout the separator tank. Notably, the remaining BTEX is prefferentially found in the distilate, indicating that these volatile compounds remain with the vapor side of the MRV process.

Figure 7-7 re-examines the overall fate of total dissolved solids. The storage reservoir and clarification have no affect on TDS concentrations. The MVR's concentrate the TDS, removing most salts from the distillate stream. The fate of calcium, magnesium, strontium, barium and boron follows that of the general TDS with most removal in the concentrate stream. Iron, however, is precipiated by the initial caustic addition in the rapid mix tank and much (90%) is removed by the clarifier. Any remaining iron is prefferentially removed in the MVR condensate.

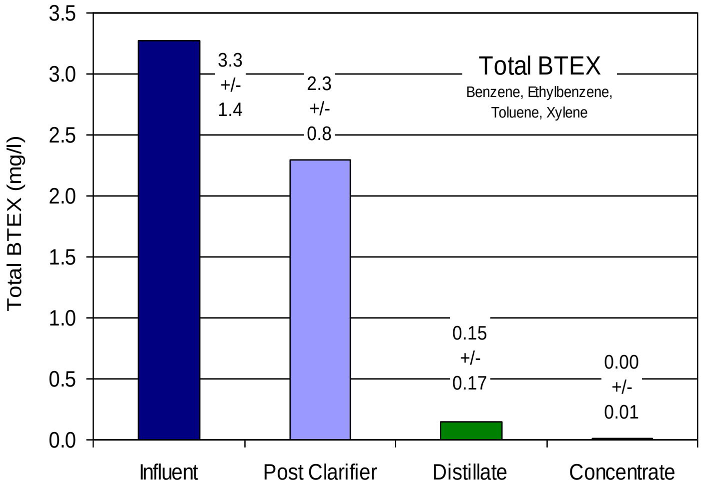

Figure 7-6: Fate of Total BETEX in the Maggie Spain Facility

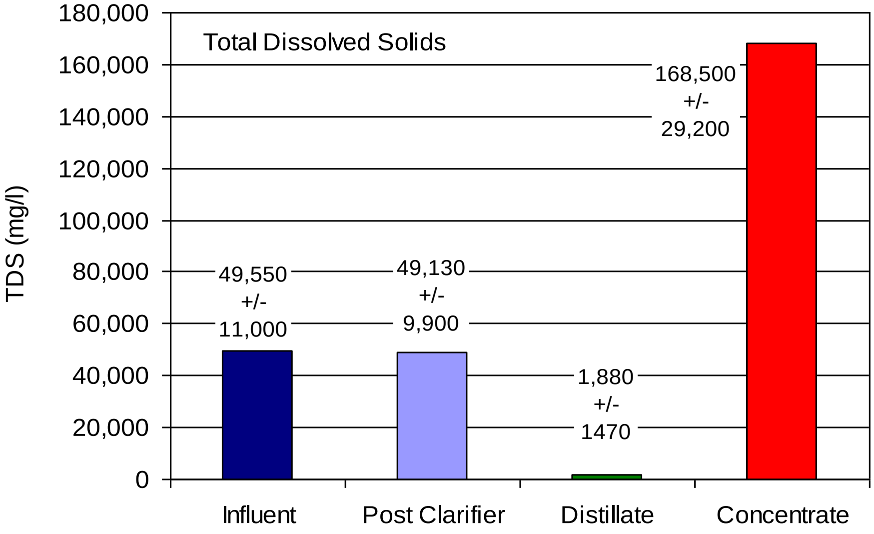

Figure 7-7: Fate of Total Dissolved Solids in the Maggie Spain Facility

Impact to Producers

Mechanical vapor recompression has been touted as an attractive alternative for the treatment of various wastewaters, expecially when water or other resource recovery is paramount. This is the case in most Barnett well fields, where fresh water is precious and deep well injection is at a premium.

The Maggie Spain facility discussed in this report is an excellent example of the MVR process as it pertains to the shale gas industry. All unit processes are mobile and can be operated on natural gas, an obvious advantage in a natural gas field. A case-in-point, this facility was moved to a new location prior to the completion of this report.

Advantages of the process are obvious from perusal of the analytical data. Most constituants of interest, including trace organics and multivalent metals, are effectively removed either in pretreatment, or in the distillation process. The distillate is sufficiently pure to be reused in place of fresh process water, or could be discharged to a receiving stream with little or no additional conditioning. The concentrate volume represents less than 28% of the original volume, resulting in lowered ultimate disposal costs.

One disadvantage of the process is the production of solid waste generated from the clarifier solids. This requires some operational expertise and maintenance time, plus additional landfill costs.

The overall treatment (entire facility) requires 72 SFC per barrel treated, or 100 SCF per barrel distillate produced. MVR costs are more difficult to detail from the data as collected. However, best-fit correlations indicate that there is a base natural gas load to the facility requiring 120-140 thousand SCF per day. Energy need per incremental barrel of treating influent water and per barrel of distillate generated was estimated to be 48 SCF and 60.5 SCF, respectively. Assuming 35% efficiency of electrical power generation from natural gas, the energy requirement is about 6.4 kWh/barrel distillate. The Maggie Spain Facility energy demand in the processing of shale gas waters appears to be as favorably low as the most efficient MVR processing cited in the literature for the treatment of far less aggressive waters in terms of organics and scale forming constituents.

As with the implementation of many water treatment processes, the “per-barrel” pricing for shale gas water treated in the mechanical vapor recompression water reclamation facility depends upon setting and a number of factors (e.g. overall water quality, average salinity of feed waters, actual deliveries of water versus capacity, year-by-year projection of flowback and produced water deliveries, etc.) that affect the efficiency and nature of the operation.

Fountain Quail pioneered shale gas water recycling in the Barnett Shale alongside some of the earliest pioneers in shale gas development. Devon Energy acquired Mitchell Energy and George Mitchell is recognized as the spark that ignited the explosive shale development in North America. The ability to adapt and react to the changing needs of this rapidly developing new industry is critical.

In order to make recycling cost competitive to disposal in the Barnett Shale (recognized as one of the lowest cost shale plays for disposal), Fountain Quail evaluates each and every cost associated with recycling in an effort to reduce costs and increase efficiency. As such, Fountain Qail often reduces the chemical costs and increases the cleaning frequency to achieve a lower cost of operation.

A very practical "oilfield-type" approach to recycling as been enacted: the equipment must be rugged, durable and easy to clean. One cannot afford to complain to the customer when an upset occurs (unexpected water composition, etc). The name of the game is to get back operational quickly. The equipment is designed with this in mind. For example, compressor efficiency was sacrificed by intentionally selecting a low speed engine-driven compressor which is very rugged and durable.

Continuous improvement has also been made. If a certain piece of equipment (i.e.: pump) causes significant downtime then it is replaced with a different design so that the overall runtime and efficiency of the system is improved. By remaining competitive in the Barnett Shale, Fountain Quail has developed a wealth of experience and knowledge that has allowed the company to expand into the Marcellus and Eagle Ford shales with NOMAD technology. For example, a new TSS-removal system called the ROVER has been developed, which is able to clean up brine for re-use where customers do not require fresh (distilled) water. The design for the ROVER is based on all the years of testing and trials of different equipment with Devon Energy in the Barnett Shale. Fountain Quail maintains that recycling must be simple, rugged, proven and cost-effective. ROVER treatment is generally <$1/bbl and NOMAD treatment can be from $3-$5/bbl, including labor, chemical and equipment.

Deliverables

Topical Report: Hayes, T.D., and Severin, B.F., Engineering Decision Tool for the Evaluation of Mechanical Vapor Recompression for the Treatment of Shale Gas Flowback Water. RPSEA Report No. 08122-05.11. February 2012.

Completed Manuscript to be Submitted to SPE in 2012

Hayes, T.D., B. Halldorson, P. Horner, J. Ewing, J.R. Werline, and B.F. Severin. Evaluation of Mechanical Vapor Recompression for the Treatment of Shale Gas Flowback Water.

Conclusions and Recommendations

The Fountain Quail design of mechanical vapor recompression represents a highly reliable process for the efficient recovery of demineralized water from concentrated shale gas brines. A demineralized water recovery averaging 72.5% or more may be operationally sustained with minimal down time due to fouling. The strength of this process is in its ability to handle influent brines of a wide concentration range. The process will achieve good recoveries of demineralized water at influent brine levels that are well above 70,000 mg/l, far above levels that are not treatable with membrane processes. This report is part of an overall effort to advise and support the natural gas industry in the evaluation and selection of treatment equipment and processes for the treatment and reuse of water used and generated by the industry. This report presents process data on a full-scale (6,000-6,800 bbl/day) mechanical vapor recompression distillation (MVR) processing plant treating shale gas hydro-fracture flowback and produced water in North Central Texas (Barnett shale region).

This investigation provided meaningful chemical and economic data concerning the MVR process. Process data were collected during a 60 day period during summer 2011. The pretreatment at this plant included caustic addition and clarification for total suspended solids and iron control. Pretreated water was distilled with three Aqua Pure MVR units, each rated at 2,000-2500 bbl/day. Distilled water recovery averaged 72.5% of the influent to the MVR's The influent total dissolved solids (TDS) fed to the MVR's averaged just under 50,000 mg/l. More than 99% of the TDS was captured in the concentrate stream. The distillate averaged 171 mg/l TDS. The fate of multivalent cations, total petroleum hydrocarbons (TPH), and BTEX) was followed. Most of the iron (90%) and TPH removal (84%) occurred in the clarification step. The removal of iron, magnesium, calcium, barium, and boron from the distillate exceeded 99%. BTEX removal from the distillate exceeded 95%.

The power at the facility was provided by two natural gas generators, making isolation of the MVR energy requirements problematic. The overall treatment (entire facility) required72 SFC per barrel treated, or 100 SCF per barrel distillate produced.   Best-fit correlations between treated water and distillate production versus natural gas utilization indicated that there was a base power load throughout the facility of about 120-140 thousand standard cubic feet of gas per day. Incremental power requirements above the baseline were approximately 48 SCF per barrel influent water treated (or 60.5 SCF per barrel distillate produced).

Implications

Outlook The implementation of MVR technology for shale gas development appears to becoming more widespread. Since the writing of this report, the mobile Maggie Spain facility has moved elsewhere within the Barnett region to provide treatment services. A similar NOMAD MVR system has begun operation in the Marcellus. Competing companies are beginning to provide similar services.

Value This report presents process data on a full-scale (6,000-6,800 bbl/day) mechanical vapor recompression distillation (MVR) processing plant treating shale gas hydro-fracture flowback and produced water in North Central Texas (Barnett shale region).   The data generated in this project are available for industry engineers to peruse and evaluate to make rational process decisions regarding MVR implementation and costing.

The MVR process may also have substantial value in plays, such as the Marcellus, where limited availability of Class II wells and long distances to the disposal wells of Eastern Ohio are already incurring costs of more than $11/bbl for disposal for brines. When reuse opportunities are depleted in many of the development areas of Pennsylvania (due to declining completions in the future), MVR processing will become of high value in achieving efficient reductions in volumes of concentrated brines, requiring only a few dollars to achieve even greater savings in reduced transportation and disposal expenditures.

Future Considerations: The Maggie Spain facility represents one solution to some of the water treatment challenges facing the natural gas industry going forward. This facility implemented preconditioning and mechanical vapor recompression as the sole demineralization process. In the future, improved membrane technologies, such as reverse osmosis or electrodialysis, may be beneficial in terms of achieving very low cost dewatering of moderate TDS brines before processing with the more energy-intensive MVR; this hybrid process would further reduce the overall cost of demineralizing shale gas brines.

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8 Evaluation of Electrodialysis for the Desalinization of Flowback Waters from Shale Fracture

Rationale

Long-term water management in the shale gas industry will depend heavily on water reuse. Certain treatment processes, such as electrodialysis, will eventually be employed by the industry to meet this need. This task was undertaken to provide initial insights into the engineering challenges, process requirements, and economic viability to treat a targeted fraction of flowback waters with electrodialysis.

Objectives

Electrodialysis is an electronically driven membrane process for the separation of salts from water. Flowback waters present unique chemical characteristics, such as extremely high concentrations of dissolved solids including calcium, barium, magnesium, and iron, not normally treated by the electrodialysis process. Electrodialysis is known to be highly susceptible to these scale forming cations. The objective of this task was to determine the technical and economic feasibility of using electrodialysis as a desalination process in such an aggressive environment. This necessitated the development of a series of engineered strategies and process improvements in order to maintain process efficiency.

Goals

As the project developed, the specific goals were refined and refocused to develop a general engineering analysis of this technology as applied to treating flowback water. Specific problems were addressed as they were encountered, and several process improvements were developed as intellectual property (see Severin and Hayes – RPSEA Report No. 08122-05.12, 2012). The generic goals and summary findings are presented below.

1. *Determine baseline operation in salt solutions of 30,000 to 60,000 mg/l TDS.*
2. ED is capable of routinely removing 20,000 – 40,000 mg/l from the diluate stream.
3. *Determine an operation range at acceptably low energy utilization.* An energy utilization of 0.1-0.14 kWh/lb salt removed can be routinely met under laboratory conditions.
4. *Determine any process improvements to increase production.* Increasing the electrolyte concentration and minimizing the overvoltage can result in up to 30% rate improvements. Temperature control of the electrolyte can result in an additional 15% rate improvement.
5. *Determine potential operational problems and provide engineering solutions.* Using field water samples from the Marcellus and the Barnett and lab generated waters, it was determined that calcium interference can be mitigated by protecting the cathode with a multivalent cation exclusionary membrane. Barium can be mitigated with a clean-in-place pole reversal process.

6. *Establish the niche for ED in a treatment process.* Pretreatment is essential to remove suspended solids and iron. With improved electrolyte, cathode protection, and clean-in place technology, the ED process can routinely provide a concentrate stream at 60,000 mg/l and diluate at 10,000 mg/l. Calcium, barium, magnesium, and iron are preferentially concentrated in the concentrate stream.
7. *Establish scale-up and economic information for field application:*
8. Operational costs of $35-40 and capital costs of $30-45 per 1000 lb salt removed are expected. The majority of the operational cost (75%) was determined to be electric power to operate the electrodes. Capital costs were dominated (>80%) by the cost of the ED stacks.

Approach

The general approach to the project was taken in four broad phases:

Phase I: Provide theoretical modeling specific to the lab scale pilot ED unit sufficient to guide the direction of the initial experiments. Predetermine the operating conditions to meet an aggressively low energy demand (0.1-0.15 kWh/lb TDS removed) for a range 30,000 – 60,000 mg/l sodium chloride.

Phase II: Determine the influence of extreme concentrations of soluble calcium (1000-4000 mg/l) as surrogate for barium and magnesium and other multivalent cations on the electrodialysis process.

Phase III: Investigate any operational problems and pretreatment needs associated with increased salt complexity, culminating in the treatment of field waters from the Marcellus and the Barnett.

Phase IV: Provide systems modeling for guidance in the placement of ED within a treatment train. Provide economic data sufficient for preliminary engineering.

The use of ED as a treatment option is being considered in context to a treatment train, such as the simplified flowchart in Figure 8-1. In this example, moderately concentrated waters of 3% to 5% TDS are treated with a membrane, such as reverse osmosis, or electrodialysis to produce a diluate stream for reuse. The concentrate stream is sent to an evaporator. The concentrate from the evaporator could be deep well injected.

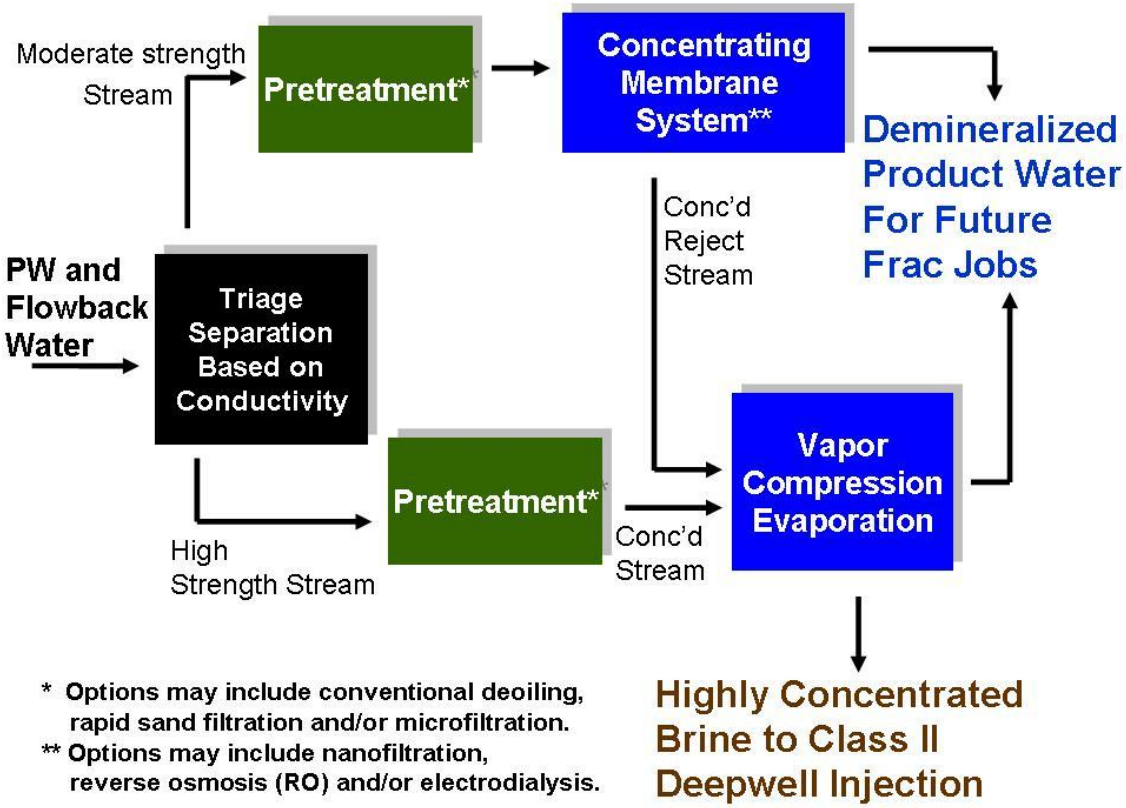


Figure 8-1: Conceptual Placement of Electrodialysis (Concentrating Membrane System) in a Water Treatment Process

Electrodialysis is an electrically driven membrane separation technology containing four distinct operational components; 1) Multiple pairs of cation and ion selective membrane are collectively called the stack; 2) A pair of hydraulic paths to collect demineralized water (the diluate stream) and the concentrated water (the concentrate stream); 3) A pair of electrode cells; one containing the anode and the second containing the cathode; and 4) An electrolyte reservoir and hydraulics to provide anolyte and catholyte. A generic depiction of the electrodialysis process is presented in Figure 8-2. As shown here, the cathode is to the right and the anode to the left. Therefore, the cations move toward the right while anions move toward the left. The pattern of alternating cation and anion selective membrane creates a pattern of alternating concentrate and diluate streams.

Equipment:

This project was performed using an Eurodia Industrie, S.A (Rungis, France) Ameridia Eur2B-10 electrodialysis pilot plant (Figure 8-3). The main component is the Eur2B-10 Electrodialysis Dialysis Stack that consists of twenty-one alternating cationic and anionic selective membranes, beginning and ending with cationic selective membranes. All anionic selective membranes were supplied by the vendor. In the first portion of this project, all cationic selective membranes were supplied by the vendor. In the final portion of this project, the single cation selective membrane at the cathode boundary was replaced with a cation selective, multi-valent exclusionary membrane. Individual membranes have an area of 200 cm^2.

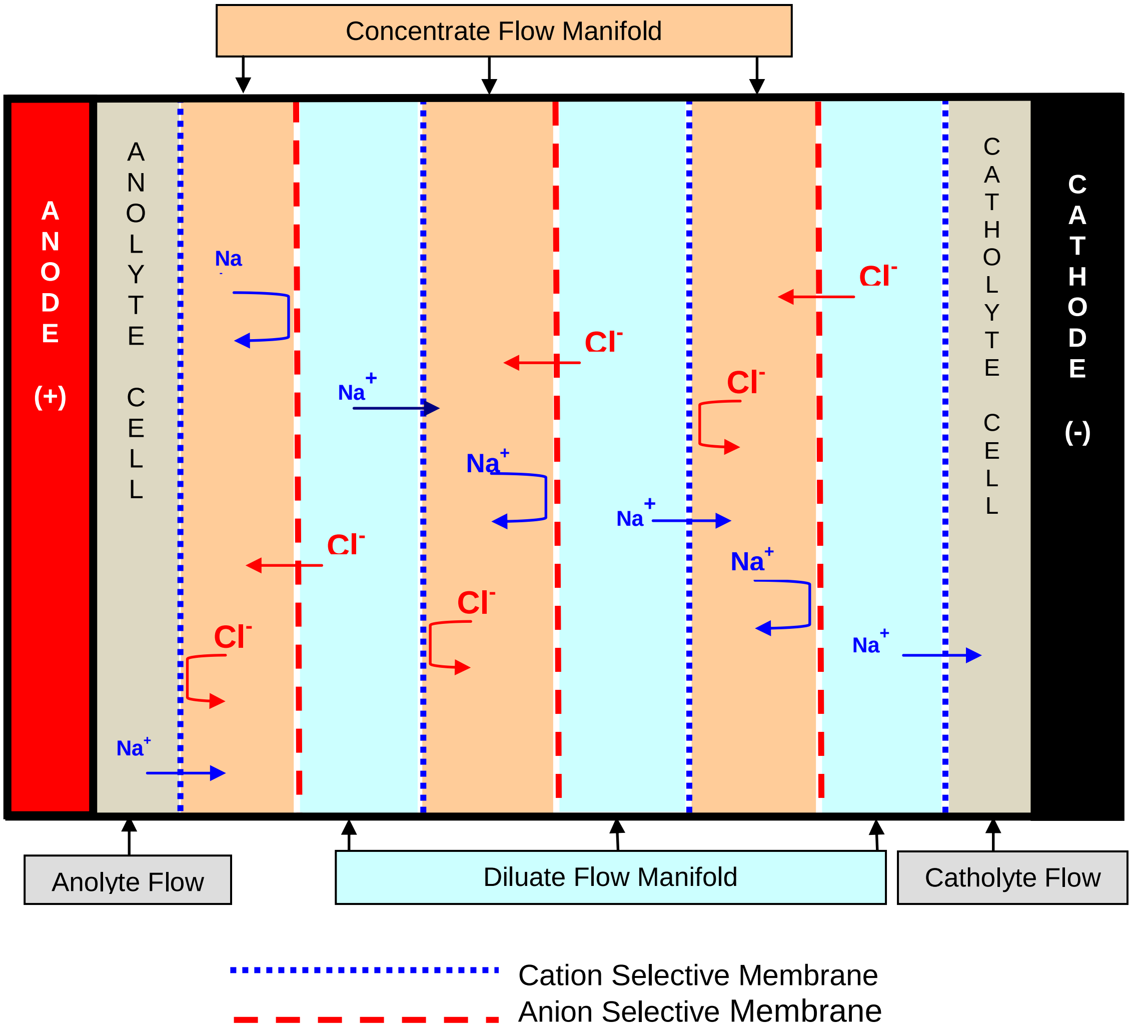


Figure 8-2: Ion Flow in an Electrodialysis Stack

The ED unit is operated in a semi-batch mode. At initiation, feed water is distributed equally to a diluate tank and a concentrate tank, each with 10 L operating volume plus associated 0.5L pipe and pump volumes. As the water is treated, salt is transferred from the diluate to the concentrate.

The electrolyte is recycled through the stack from a common pump that distributes both the anolyte feed and the catholyte feed. The returned anolyte and catholyte pass through a split tank (total active volume 10 L + 1L) with stilling wells to dissipate collected hydrogen gas (catholyte side) and oxygen gas (anolyte side).

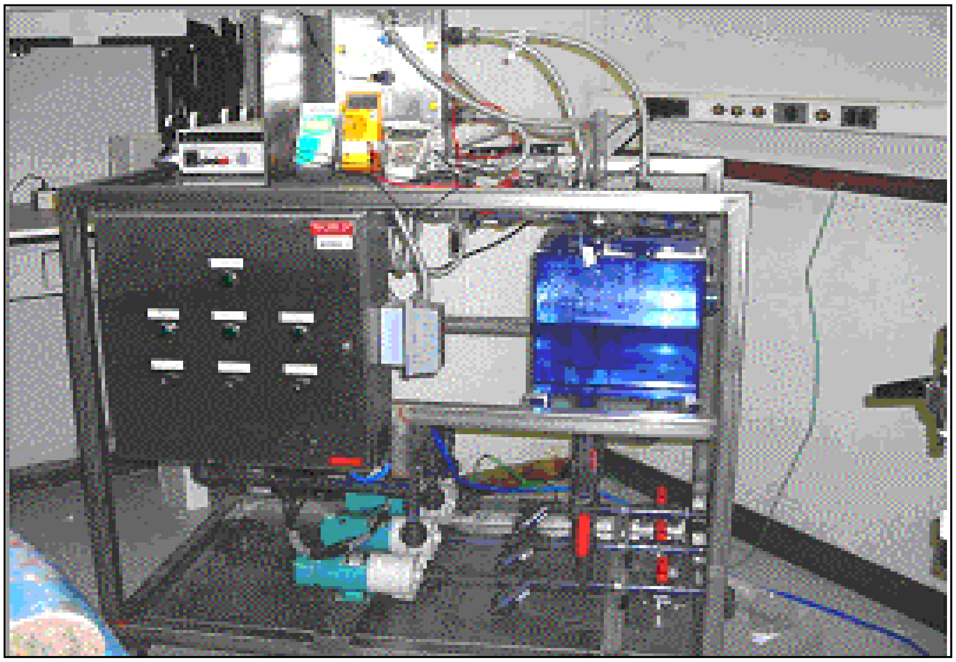


Figure 8-3: Photograph of the Eurodia Pilot ED Skid

Continuous runs were performed by filling the diluate and concentrate tank each with about 10.5 liters of the desired feed water. The electrolyte tank was filled with 10.5 liters of the desired electrolyte. In the tests reported, herein, the electrolyte was 90 g/L disodium sulfate, or as noted otherwise.

When in continuous-mode, the instruments were polled once every minute by data collection software. The master software was Labview (National Instruments) written by a GTI engineer. Oakton Instruments Con 110 meters (Oakton Instrument Company, Vernon Hills, IL) were used to continuously measure conductivity and temperature in the diluate and concentrate tanks. The conductivity meters were calibrated by setting all meters to a 12.50 mS/cm (milli-Semens per centimeter) standard (Oakton Instruments). Subsequently, a series of sodium chloride solutions ranging from 120,000 mg/l to about 8000 mg/l NaCl were prepared. Calibrations were regenerated each week of testing and spot checked against a single solution daily during a week of testing. Three Oakton Instruments pH 110 meters (Oakton Instrument Company, Vernon Hills, IL) were occasionally used to measure the pH of the diluate, the concentrate, and the electrolyte. The power source was equipped with a computer interface. The potential (DC volts) and current (amperage) were polled every minute by the Labview software. All continuous runs were performed at 5 V stack potential.

Chemical tests for specific cations and anions were performed under contract with an outside contractor (STAT Analysis Corportion, Chicago, IL). The samples were tested by ion chromatography for sodium, barium, chloride, sulfate, and calcium, magnesium, manganese, and iron.

Results and Discussions

Define a Range of Operation: An arbitrary energy utilization limit (0.1 to 0.15 kWh/lb TDS removed) was established to keep the electrical costs of electrodialysis at less than $0.18 per barrel of flowback water treated. Energy utilization was calculated for 33 electrodialysis runs, including 11 tests with field samples from the Marcellus and the Barnett (Figure 8-4). The average energy expended was 0.12 kWh/lb TDS with a range from 0.1 to 0.148 kWh/lb.

Chemistry of the Electrolyte: The chemistry of the electrolyte solution was investigated as a means of improving the rate of salt transfer at the desired stack potential. Increasing the electrolyte concentration to an ionic strength similar to the water being improved the process by as much as 24%.

Mitigating the Effects of Calcium: Calcium concentrations greater than several hundred mg/l have traditionally been a problem with electrodialysis. Flowback water contains calcium at levels exceeding several thousand mg/l. The apparent calcium fouling (in and around) the electrode cells was indicated by a rapid degradation of process efficiency. The single cathode boundary membrane was replaced with a membrane that selected against multivalent cations. Calcium flux into the electrolyte was reduced by 66-73%, with an improvement in ion flux of about 40% compared to the baseline observations.

Interference and Fate of Multivalent Cations: Flowback water contains a variety multivalent cations, in addition to calcium, that can potentially adversely affect electrodialysis. Iron caused an immediate loss of process efficiency, likely by precipitation at all membrane surfaces. Calcium, barium, and magnesium caused a slower degradation of ion flux. Barium, iron, magnesium, and calcium were preferentially transported from the diluate to the concentrate. Calcium and magnesium were transported slowly into the electrolyte. Barium and iron were either not readily transported, or not readily measured in the electrolyte.

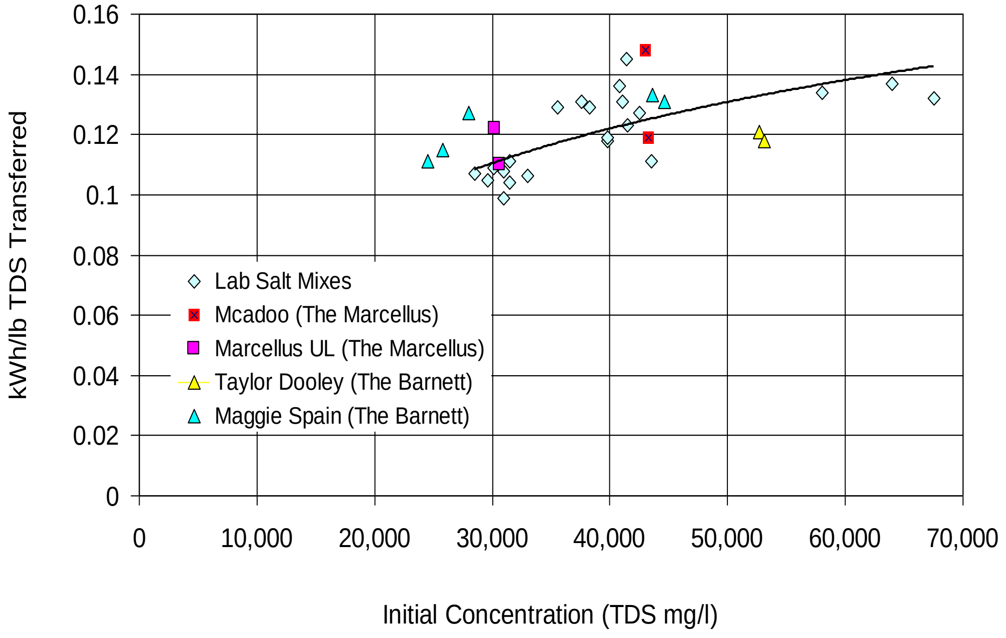


Figure 8-4: Summary of All ED Runs, Energy Utilization (Work) Required Per Pound of TDS Transferred

Clean-in-Place: Loss of process efficiency was observed when calcium, iron, and barium were present in the test water. To overcome this problem, a rapid clean-in-place regime was developed. Short pulses (15 seconds to one minute duration at intervals of 15 minutes to one hour) of pole reversal (cathode to anode) at elevated voltages (5-15 V) improved total ion flux. Tests were conducted with mixed salt solutions and field waters from the Barnett and Marcellus. Flux improvements of up to 37% were measured for waters treated using a CIP regime.

Field Waters from the Barnett and the Marcellus: Samples were received from two field sites in each the Barnett and the Marcellus (total four field samples). Pretreatment consisting of pH adjustment to neutrality, aeration, and filtration with a 5 µ cartridge filter, was sufficient to create treatable waters. In three of four cases, the water was deemed beyond the concentration suitable for effective electrodialysis (150,000 – 270,000 mg/l TDS), and likely represented water collected from late in the flowback periods at these sites. These waters were diluted with tap water for the tests with ED.

***Effect of Temperature*:** The design of the electrodialysis process creates two co-dependent, rate limiting reaction sites; the electrode cell reactions, and the transport of ions within the membrane stack. The Arrhenius equation for temperature dependency was modified for two co-dependent rates over a temperature range of 8°C to 33°C. Independent temperature coefficients for the electrode cells and the stack were obtained. These tests predict that field operation can be improved with increased operating temperature. Significant improvements (>15%) may be made by increasing the electrolyte temperature.

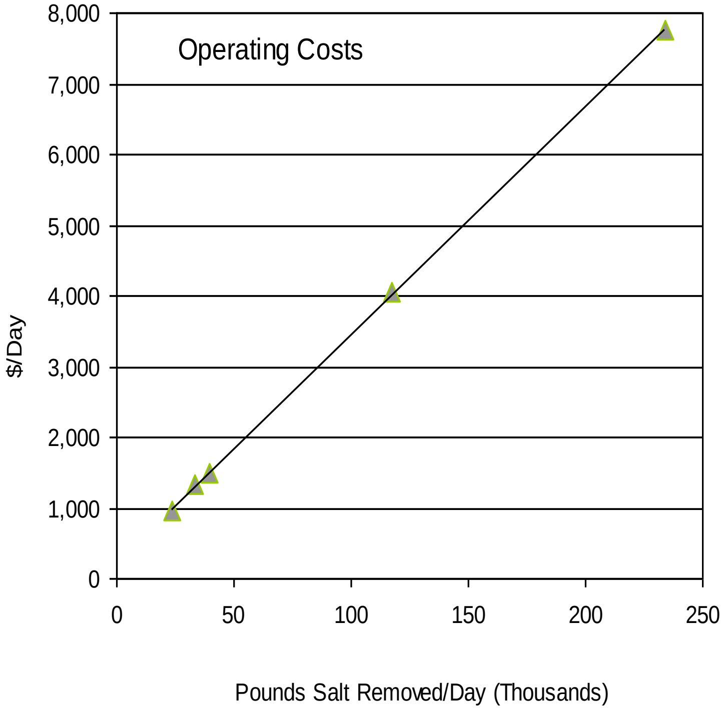
Process Recommendations: Iron should be aggressively removed in pre-treatment. Increased concentration of electrolyte can improve the process by around 24%. If the level of calcium and iron is fairly low, then the pH of the electrolyte can be increased to pH 11 for an additional 15% improvement in the rate of the process. With high concentrations of calcium, protection of the cathode barrier membrane with a multivalent cation exclusionary membrane is imperative. Improvements of 40% are possible. Clean-in-place technology will be needed to keep the ED unit operational. For very little expenditure, 35% process improvement can be realized using a simple pulsed pole reversal. The use of waste heat to increase the temperature of the electrolyte, the water, or both, can improve the rate of the process by at least 15%.

Process Economics: Eurodia provided a set of capital and operational parameters for specific design examples (Table 8-1). The design parameters were converted, with additional assumptions, into cost estimates. A typical design case resulted in an operational cost of about $35-40/ 1000 lb salt removed. The majority of the operational cost (75%) was determined to be electric power to operate the electrodes. Power costs were estimated at $0.10/kWh. Membrane replacement and labor accounted equally for 20-25% of the costs. Pumping costs and chemical cleaning agents were nominal, compared to the other operational costs. Figure 8-5 suggests that operating costs are linear with respect to the mass of salt removed per day.

Table 8-1. Test Cases for Economic Analysis

Test Case	A3	A4	A5	A6	B1	B2	B3
Inlet TDS	70,000	40,000	20,000	10,000	40,000	40,000	40,000
Effluent TDS	40,000	10,000	10,000	1,000	10,000	10,000	10,000
BBL/d treated	10,000	10,000	10,000	10,000	50,000	20,000	2,000
1000 Lb Salt/Day removed	117	117	40	34	586	234	23

Capital costs were amortized for 7 years and 7% interest to estimate a capital cost per 1000 pounds salt removed. A typical design case resulted in a capital cost of $30-45/1000 lb salt removed. Capital costs were dominated (>80%) by the process equipment for the electrodialysis unit. Placeholder costs estimates for generators and construction (building and site preparation) accounted for about 20% of the required capital. Figure 8-6 suggests that capital costs are linear with respect to the mass of salt removed per day. A further comparison between the process data in this report and the estimates from Eurodia suggests increased capital costs (dominated by the cost of the electrodialysis equipment), can be offset by lower operating costs (dominated by energy requirements).



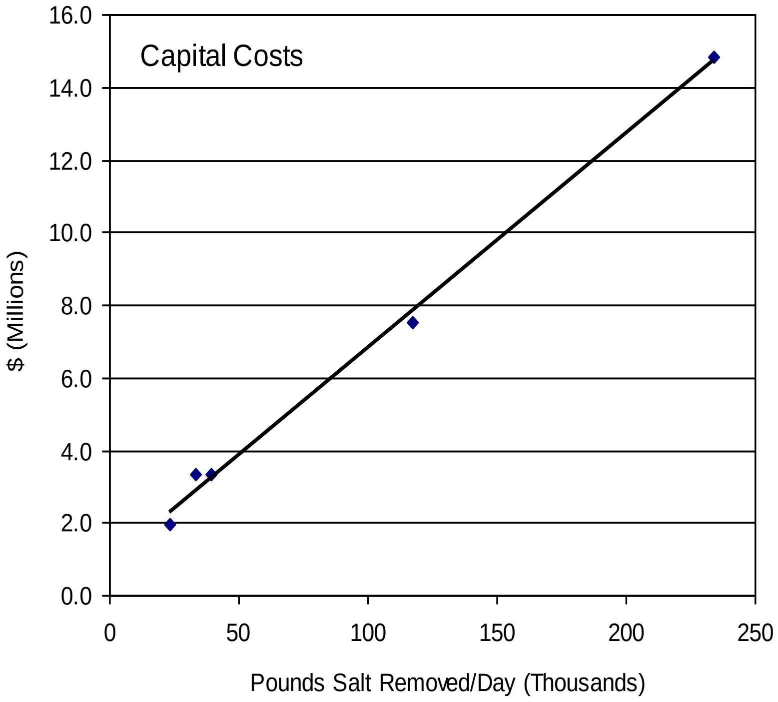


Figure 8-5: Capital Costs as a Function of Daily Salt Removal (right)
Figure 8-6: Operating Costs as a Function of Salt Removal (left)

Operating costs are shown in Figure 8-7 for five of the test cases. Pumping and cleaning chemical costs were combined, being minimal compared to the other costs. When presented in this manner, it can be seen that the stack power and membrane replacement costs are nearly constant on a basis of $/lb salt treated. The economy of scale appears to be in labor. Labor is a placeholder value for this evaluation.

Capital costs are shown on a case-by-case basis as a function of salt removal in Figure 8-8. Recall that these values are based on amortized capital (7 years, 7%). Economy of scale appears to stabilize between Cases A3 and A4 and Case B3, indicating that the most efficient capital use appears to be for cases that exceed 117,000 pounds of salt per day.

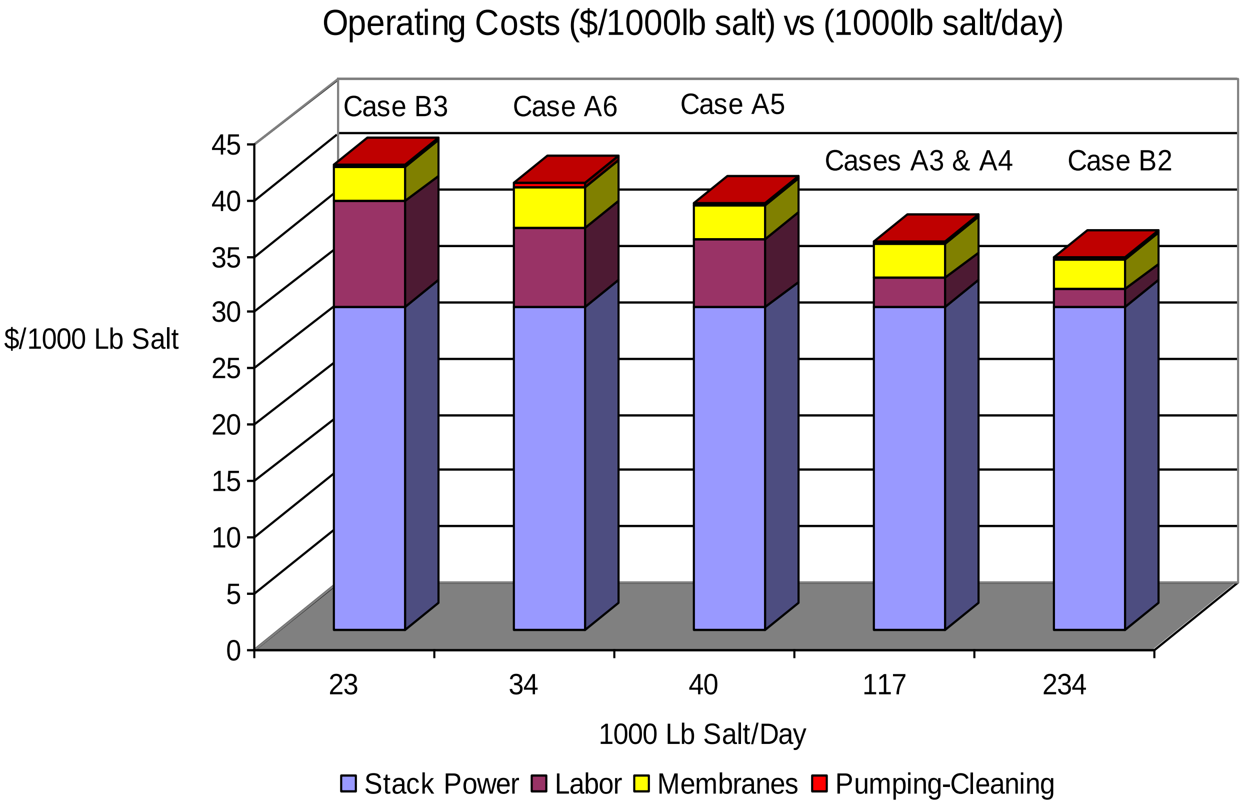


Figure 8-7: Breakdown of Operating Costs ($/1000 lb salt) as a Function of Daily Salt Removal

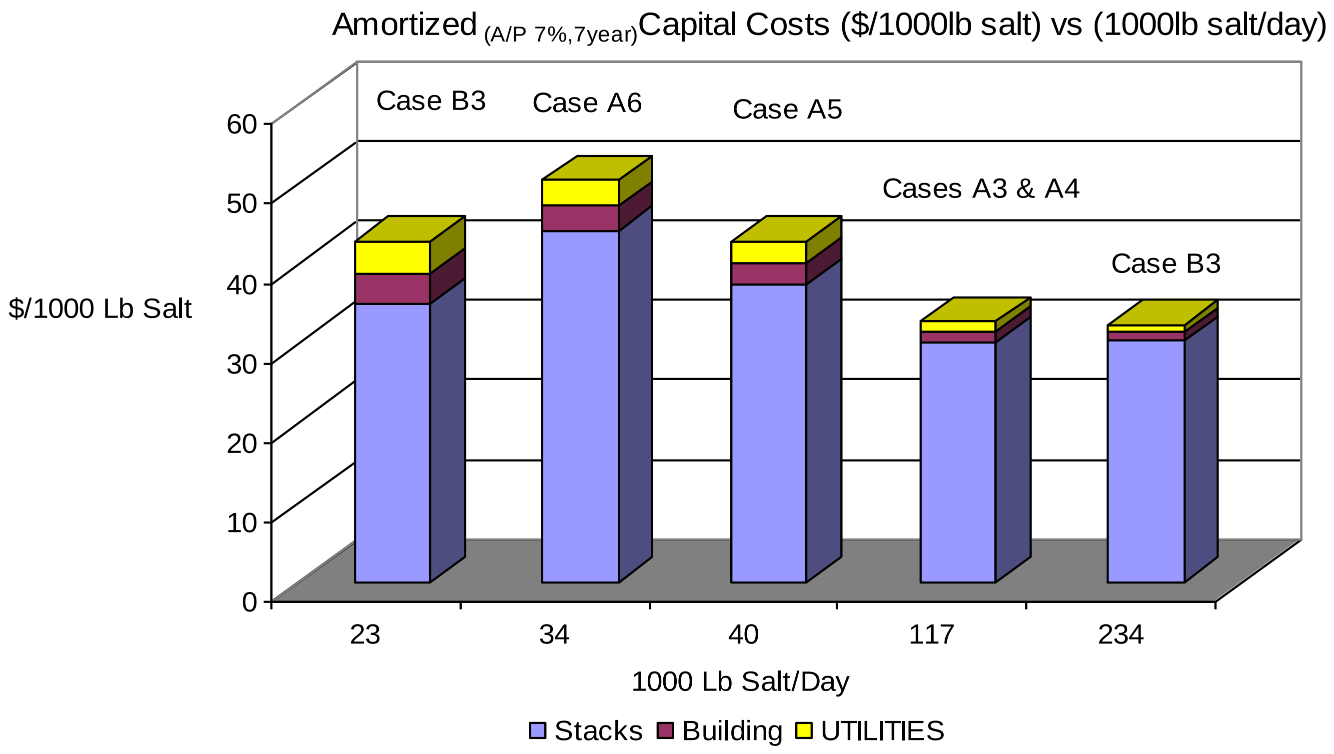


Figure 8-8: Amortized Capital Normalized ($/1000 Lb Salt Treated) versus Daily Treatment.

Deliverables

Topical Reports

Severin, B.F., and Hayes, T.D., Development of Electrodialysis for Shale Gas Water Reuse. RPSEA Report No. 08122-05.01. November 2010.

Severin, B.F., and Hayes, T.D., Evaluation of Electrodialysis in the Demineralization of Shale Gas Flowback Waters. RPSEA Report No. 08122-05.12. February 2012.

Completed Manuscripts to be Submitted to a Refereed Journal in 2012

Hayes, T.D.,and Severin, B.F., Evaluation of Electrodialysis for the Desalinization of Flowback Waters from Shale Fracture: Part I, Problem Definition.

Hayes, T.D., and Severin, B.F, Evaluation of Electrodialysis for the Desalinization of Flowback Waters from Shale Fracture: Part II, Field Samples.

Hayes, T.D. and Severin,B.F., Evaluation of Electrodialysis for the Desalinization of Flowback Waters from Shale Fracture: Part III, Interference and Fate of Multivalent Cations.

Severin, B.F.,and Hayes,T.D. Evaluation of Electrodialysis for the Desalinization of Flowback Waters from Shale Fracture: Part IV, Effect of Temperature

Invention Disclosures

Intellectual Property Disclosure I: Hayes, T.D., and Severin, B.F., Clean-in-Place Method for Electrodiaslysis Electrode Cells.

Intellectual Property Disclosure II: Severin, B.F., and Hayes, T.D., High Rate Electrodialysis by Electrolyte Temperature Control.

Intellectual Property Disclosure III: Severin, B.F., and Hayes, T.D., Divalent Cation Exclusion from Electrolyte Solutions in the Electrodialysis Process; The Scavenger Cell

Intellectual Property Disclosure IV: Hayes, T.D., and Severin. B.F., Mitigation of High Calcium and Other Multivalent Cation Concentrations on the Treatment of Highly Concentrated Brines with Electrodialysis.

Intellectual Property Disclosure V: Hayes, T.D., and Severin, B.F. Electrolyte Chemistry Improvements for Electrodialysis of Heavy Brine

Impact to Producers

The overarching goal of this project is to provide the producers with information that helps to 1) minimize fresh water utilization, 2) maximize water reuse, 3) minimize disposal costs, and 4) reduce truck traffic (carbon footprint) throughout a gas play. Other tasks in this project investigated the chemical composition of flowback waters (Task 4 Water Characterization), the feasibility of early flowback capture (Task 5 Feasibility of Early Flowback Capture), and the long term management challenges (Task 11 Systems and Life Cycle Analysis) and how these systems impact an engineered solution, such as the flow sheet presented in Figure 8-1.

Some early flowback water may be reused directly with minimal pretreatment. A second fraction of water, with mid-range conductivity 20,000 – 50,000 mg/l, may need to receive intermediate ion separation, such as presented in this Task 8, or by other means, such as reverse osmosis (Task 9 and Task 10 Field Experimental RO Membranes). The diluate fraction from electrodialysis or reverse osmosis can be targeted to provide the quality necessary for reuse. The concentrate from electrodialysis or reverse osmosis may be further treated in a more costly process, such as mechanical vapor recompression (Task 7 Mechanical vapor Recompression).

Electrodialysis is a readily available and widely used desalination process. Results generated in this task (Task 8 Electrodialysis) suggest modifications and pretreatment needs necessary to implement this particular technology within an engineered system, such as Figure 8-1. A series of treatment cases were analyzed by the manufacturer. A typical design case resulted in an operational cost of about $35-40/1000 lb salt removed and a capital cost of $30-45/1000 lb salt removed. This yields, for example, a cost of about $1 per barrel for water at 50,000 mg/l treated to a target of 10,000 mg/l. This compares beneficially to other competing costs, such as transportation, disposal, or advanced treatment such as mechanical vapor recompression.

Conclusions and Recommendations

The treatment of flowback waters from shale gas hydrofracture with electrodialysis represented a dual technical challenge. Normal operation of electrodialysis is in the range of several thousand mg/l TDS and limited to several hundred mg/l calcium and magnesium. This project centered on 1) keeping the operating costs under a controlled limit and 2) finding opportunities to maximize process output. A number of problems were encountered that were systematically addressed as the project proceeded from the treatment of water containing pure sodium chloride (30,000-60,000 mg/l) to the treatment of solutions with sodium, calcium (up to 4,000 mg/l), barium (up to 400 mg/l), iron (up to 50 mg/l), and magnesium (up to 600 mg/l), and finally to the treatment of field samples from the Barnett and the Marcellus. Some of these improvements represent potentially scalable means for cost savings. Others of these improvements represent critical changes needed to keep the electrodialysis unit operational.

Implications

The major implications of this development effort relate to the process needs and changes required to meet the aggressive water chemistry in flowback waters.

- Iron appears to be the most likely cation to cause fouling of the ED process. Iron must be aggressively removed in pre-treatment.
- Increase the concentration of electrolyte to reduce resistance at the electrodes. This can improve rate of the ED process.
- If the level of calcium and iron is fairly low, then the pH of the electrolyte can be increased to pH 11. This reduces the overvoltage applied to the anode and can account for an additional improvement in the rate of the process.
- With high concentrations of calcium, protection of the cathode barrier membrane with a multivalent cation exclusionary membrane is imperative. Without this improvements, expect a 40% decrease in process.
- Clean-in-place technology will be needed to keep the ED unit operational for very little expenditure. If not implemented, expect a 35% decrease in process.
- The use of waste heat to increase the temperature of the electrolyte, the water, or both, can improve the rate of the process by at least 15%.

Outlook The implementation of electrodialysis into an engineered water reuse systems appears economically feasible with and estimated cost of about $1 per barrel for water at 50,000 mg/l treated to a target of 10,000 mg/l. Globally, electrodialysis is increasingly used for demineralization purposes in the food, chemicals and water reclamation industries; it is likely that the process will gain greater visibility in the handling of produced and flowback waters of the shale gas industry, as well. Successful entry into the shale gas market will depend on the completion of development of the ED process to incorporate the five process improvements that were developed in this project. Further R&D will enhance the technology's probability of success.

Value The value of the ED process lies in its ability to recover low TDS water from moderately concentrated brine before introducing the concentrated brine to the more energy and capital intensive thermal separations processes. The data generated in this project are available for industry engineers to peruse and evaluate as a part of rational decision making.

Future Consideration A number of process improvements have been suggested to make electrodialysis field ready. These include intellectual property issues:

1. A Clean-in-Place Method for Electrodiaslysis Electrode Cells.
2. Improved High Rate Electrodialysis by Electrolyte Temperature Control.
3. Divalent Cation Exclusion from Electrolyte Solutions in the Electrodialysis Process with a Scavenger Cell.
4. Mitigation of High Calcium and Other Multivalent Cation Concentrations on the Treatment of Highly Concentrated Brines with Electrodialysis.
5. Electrolyte Chemistry Improvements for Electrodialysis of Heavy Brine.

These IP positions were conceived based on work performed in this project. While some of these were reduced to practice in the small lab unit used in this project, a future consideration would be to more fully develop these concepts in this lab unit and potentially larger units robust enough for an evaluation under actual field conditions.

9 Novel Fouling—Resistant Membranes for Barnett Shale Water Management and Reuse Technologies

Rationale

Hydraulic fracturing, used in the production of natural gas from the unconventional gas shales, requires large quantities of water. Challenges for extensively employing hydraulic fracturing include, among others, the availability of water and the management of produced and flowback waters from well completion. These challenges can be mitigated by reusing produced and flowback waters. Long-term water management in the shale gas industry will depend heavily on water reuse. Certain treatment processes, such as electrodialysis, will eventually be employed by the industry to meet this need. This task was undertaken to provide initial insights into the engineering challenges, process requirements, and economic viability to treat a targeted fraction of flowback waters with electrodialysis.

Objective

A major challenge in purifying produced water with membranes is fouling. Produced or flowback water is typically composed of dispersed oil, organics, salts, metals, and treatment chemicals[1], which badly foul the membranes. The accumulation of foreign materials on the membrane hinders the flow of water through the membrane, which in turn drives up the cost of operation[2]. Membrane surface modification can be used to improve fouling resistance of membranes[3]. By increasing surface hydrophilicity, reducing surface charge, and reducing surface roughness, membrane fouling can be reduced[3]. In this study, polydopamine, a hydrophilic surface modification material, was used to reduce membrane fouling by oil/water emulsions. Influence of the modification conditions on membrane performance was investigated.

Goals

The goals of this task were to:

1. Demonstrate the baseline performance of commercial ultrafiltration, nanofiltration and reverse osmosis membranes in the removal of constituents of interest from shale gas waters.
2. Modify these membranes with coatings selected to minimize fouling and improve energy efficiency.
3. Demonstrate improved membrane performance under laboratory conditions.

Approach

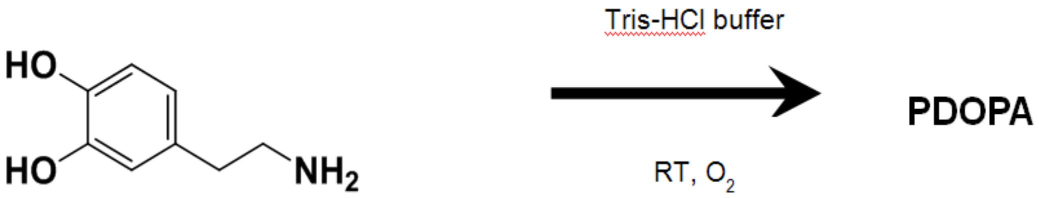
Membrane Selection: Produced or flowback water often contains sufficient levels of salt to require desalination prior to reuse or surface discharge, and reverse osmosis (RO) membranes are commonly used to desalinate water. Pretreatment, employing ultrafiltration (UF) membranes, reduces fouling in RO membranes by removing oil, grease, suspended solids, and other large molecules prior to RO treatment. Commercial RO and UF membranes were, therefore, the major focus of this research; the specific membranes considered in this study are listed in Table 9-1.

Table 9-1: Commercial Membranes Used in the Fouling Tests

Classification	Membrane Polymer	Manufacturer	Pore Size	Pure water Flux (LMH/bar)	Study ID
UF	Polysulfone	Sepro (PS-20)	~20 kDa[1] MWCO[2]	1000	PS-20 UF
UF	Polyethersulfone	Sepro (PES-30)	~20 kDa MWCO	300	PES UF
NF	Polyamide	Dow (NF-90)	N/A	12.3	PA NF-90
RO	Polyamide	Dow (XLE RO)	N/A	7.7	PA XLERO

1. KDa = 1000 Daltons Pore Size
2. MWCO = Molecular Weight Cut Off.

Membrane Surface Modification with Polydopamine (PDOPA): Surface coating with polydopamine (PDOPA) is a new approach to improve membrane fouling resistance. Dopamine in Tris-HCl buffer solution undergoes polymerization under slightly alkaline conditions to form polydopamine[4] as shown in Figure 9-1.



Dopamine

Figure 9-1: Conversion of dopamine to polydopamine (PDOPA)

Polydopamine can non-selectively deposit onto virtually any surface due to its excellent adhesion properties[4]. Since the polydopamine layer is uncharged and very hydrophilic, it helps reduce oil/grease adhesion and, in turn, membrane fouling. Moreover, PDOPA-coated membranes can be used to covalently bind other molecules such as amine-terminated poly(ethylene glycol) (PEG-NH_2) to the membrane to further help reduce membrane fouling[5]. Generally, the polydopamine can be coated as a very thin layer; thus, it has minimal effect on membrane flux.

Membrane Modification Protocol: UF and RO membranes were pretreated with isopropyl alcohol (IPA) prior to membrane coating to ensure that the pores of the membranes were open and accessible during filtration tests. The membranes were coated with PDOPA by exposing their active layers to an aqueous solution of dopamine hydrochloride in 15 mM Tris-HCl buffer. Unless otherwise stated, a dopamine concentration of 2 mg/mL, Tris-HCl buffer pH of 8.8, and

60 minute deposition time were used. Following polydopamine deposition, the membrane was soaked in ethyl alcohol (for UF membranes) or 25% (v/v) IPA (for RO membranes) for 10 minutes to remove any weakly-bonded polydopamine before being rinsed thoroughly with deionized water and stored in deionized water until used.

Methyl-terminated poly(ethylene glycol) amine (mPEG-NH_2, MW = 5 kDa) was grafted to some PDOPA-coated membranes at 60°C for 60 minutes. The grafting solution was 1 mg/mL of PEG-NH_2 in 15 mM tris-HCl buffer at pH 8.8. Membranes with grafted PEG are denoted as PDOPA-g-PEG-modified membranes in this report.

Emulsified Oil Fouling Tests: The fouling study was conducted using a constant transmembrane pressure (TMP) crossflow filtration system, as shown in Figure 9-2. The model feed foulant solution was 1500 ppm soybean oil/DC193 (non-ionic surfactant) in deionized water emulsion (with an oil to DC193 ratio of 9:1). To study salt rejection of RO membranes, 2000 ppm NaCl was added to the feed solution prior to adding the foulant solution. The UF membranes were tested at a TMP of 30 psi and a crossflow rate of 0.8 L/min (Re ~ 1000). The RO membranes were tested at a TMP of 150 psi and a crossflow rate of 3.8 L/min (Re ~ 4900).

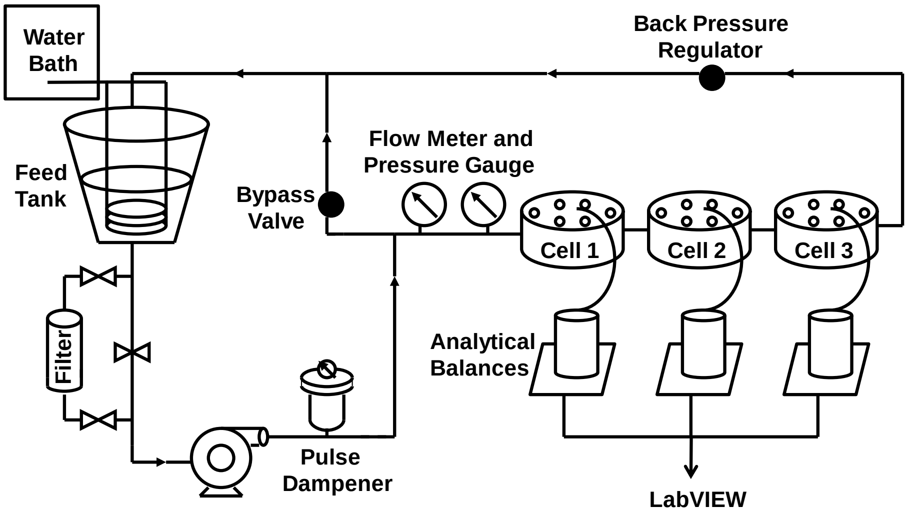


Figure 9-2: Constant TMP crossflow filtration system

Results and Discussion

Experimental results are shown in Figure 9-3. The PDOPA-modified membranes exhibited higher permeate flux (at 24 hours filtration) than the unmodified membranes in all cases. Grafting PEG-NH_2 onto the PDOPA coating slightly enhanced the permeate flux of the PS-20 and PES UF membranes relative to the PDOPA-modified (ungrafted) membranes. The RO and NF membranes, however, yielded lower permeate flux after they had been grafted with PEG-NH_2. The PEG-NH_2 coating generally increased the resistance to water transport through the membranes. For porous membranes, such as UF membranes, the increase in mass transfer resistance due to PEG grafting is small. However, membranes with very small or no pores, such as NF or RO membranes, suffer from large additional mass transfer resistance introduced by the PEG-NH_2 grafting.

Effect of Polydopamine Surface Modification Conditions: Various modification conditions were investigated: dopamine concentrations (0.1, 0.5, 2, 4, and 8 mg/mL), PDOPA deposition times (30, 60, and 120 minutes), and initial pH values of tris-HCl buffer solution (5, 8.8, and 11). The fouling behavior of modified PA XLERO membranes was evaluated at each coating condition and compared with that of unmodified membranes. The oil/water emulsion fouling tests and NaCl rejection measurements were conducted as described in the earlier section. Modified membranes were also tested for pure water flux using dead-end filtration at a TMP of 150 psi.

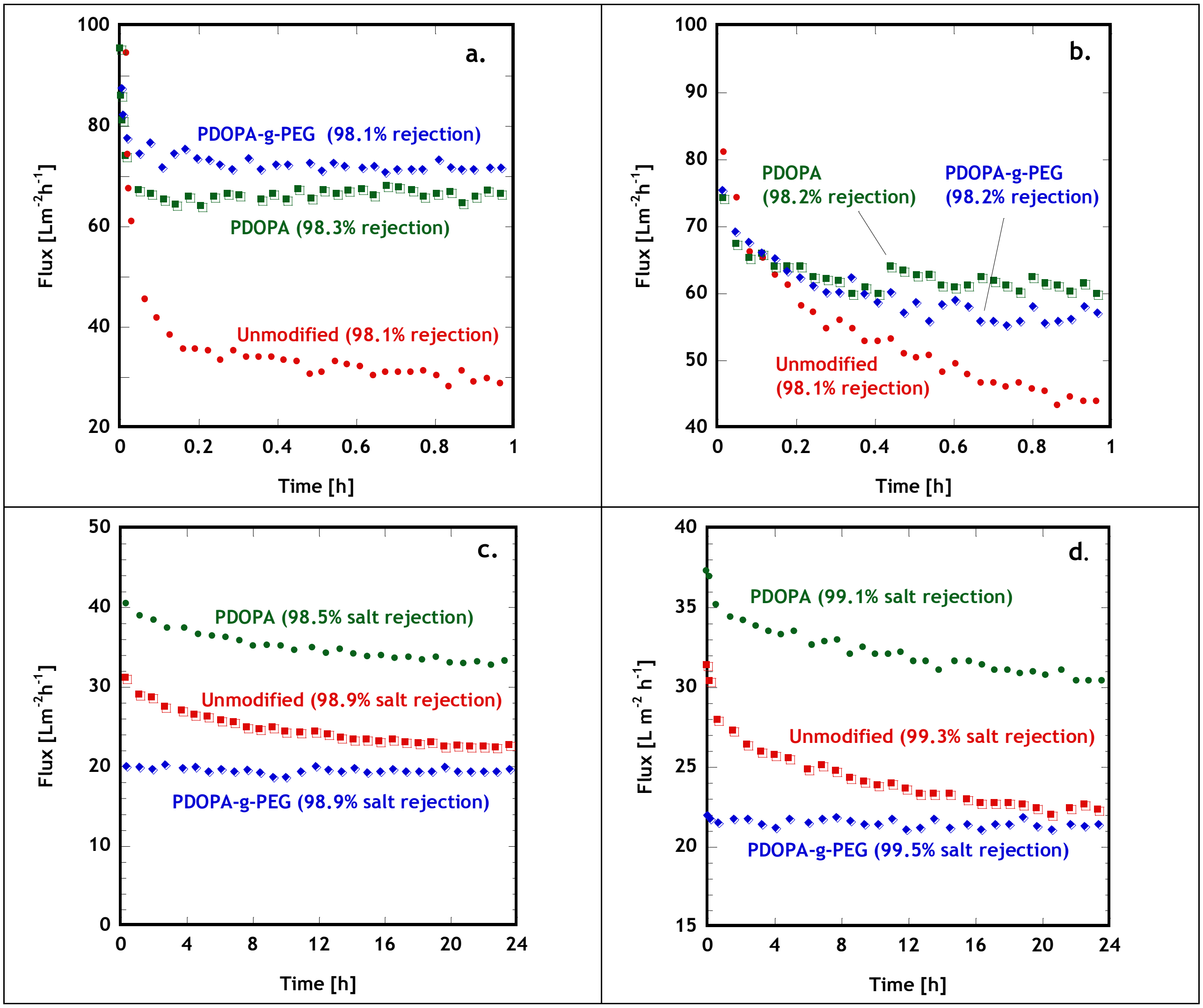


Figure 9-3: Permeate flux as a function of time in soybean oil/water emulsion filtration using unmodified, PDOPA-modified, and PDOPA-g-PEG-modified membranes. a. PS-20 UF, b. PES UF, c. NF-90, and d. PA XLERO membranes. Rejection values (organic rejection for UF membranes, salt rejection for NF and RO membranes) were measured at the end of filtration.

As shown in Figures 9-4a and 9-5a, pure water flux decreased with increasing dopamine concentration and deposition time. Higher dopamine concentrations[6]-[8] and longer coating times[4],[6]-[10] yield thicker PDOPA layers on the membrane surface. This layer creates additional mass transfer resistance which reduces the pure water flux. However, all PDOPA-modified membranes exhibited improved permeate flux relative to the unmodified membranes during fouling tests as shown in Figures 9-4b and 9-5b. Figure 9-4b shows that the membranes modified with different dopamine concentrations displayed little variation in the permeate flux during oil/water emulsion filtration. The results indicated that the mass transfer resistance due to the PDOPA coating was insignificant compared to that from the foulant layer introduced by oil emulsion. 9. 5b shows that the membranes modified with 30 minutes deposition time produced a slightly lower permeate flux than those modified for 60 and 120 minutes. This result could be due to an incomplete coverage of the coating at short deposition time (*i.e.,* 30 minutes).

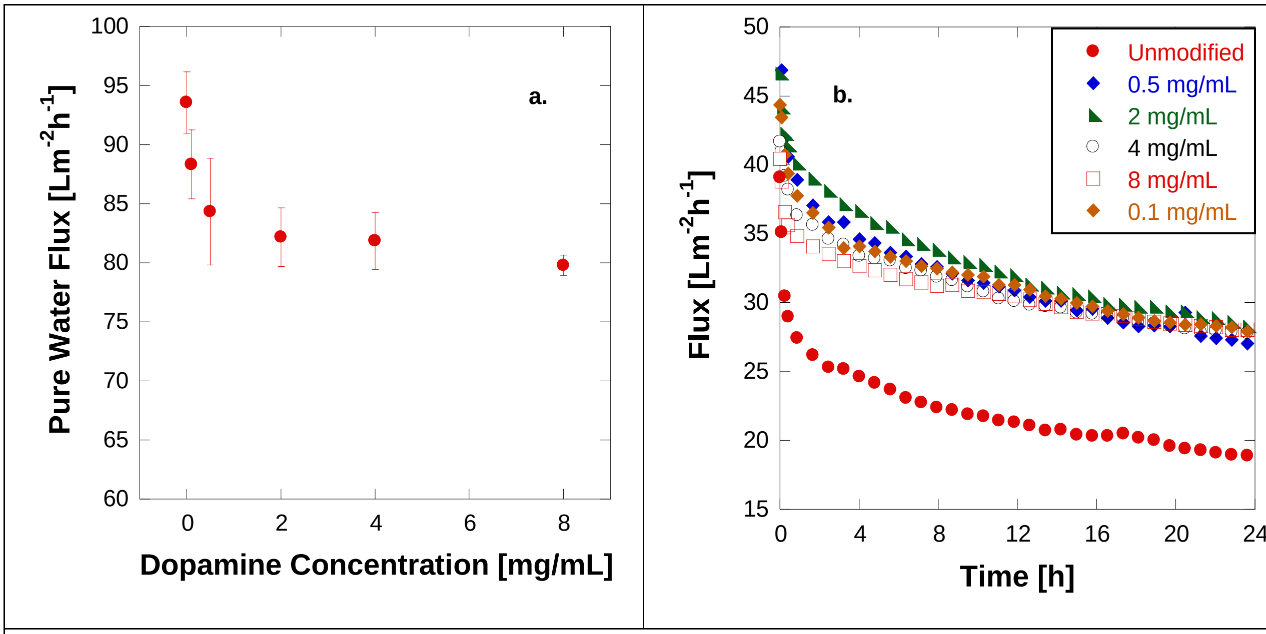


Figure 9-4: a. Pure water flux as a function of dopamine concentration used during PA XLERO membrane modification; b. Permeate flux as a function of time in soybean oil/water emulsion filtration using PA XLERO membranes unmodified and PDOPA-mcodified at different dopamine concentrations (with 60 minutes deposition time and tris-HCl buffer initial pH at 8.8).

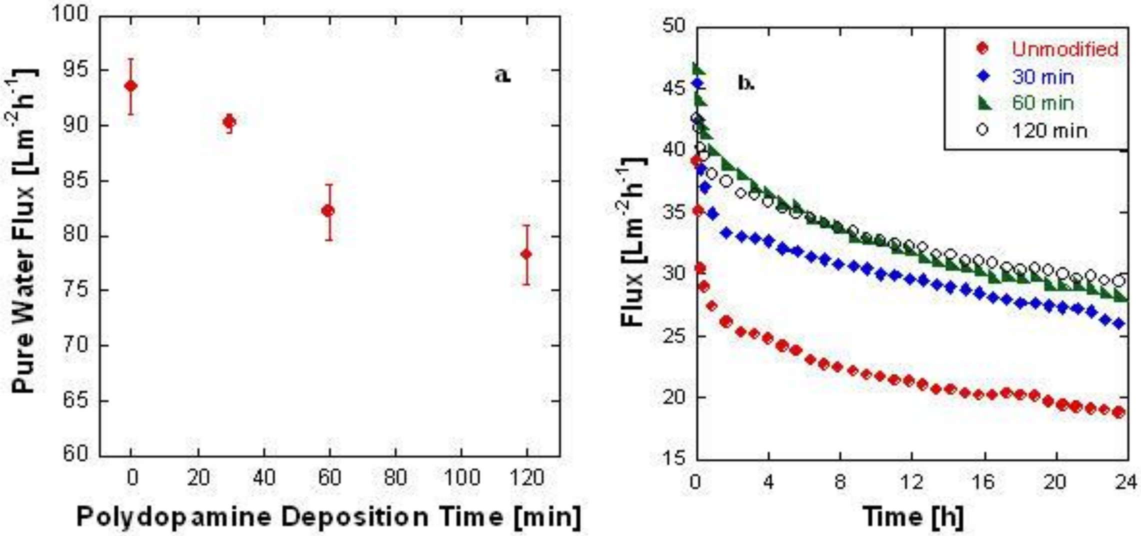


Figure 9-5: a. Pure water flux as a function of deposition time used during PA XLERO membrane modification, b. Permeate flux as a function of time in soybean oil/water emulsion filtration using PA XLERO membranes unmodified and PDOPA-modified at different deposition times (with 2 mg/mL dopamine concentration and tris-HCl buffer initial pH at 8.8).

As shown in Figure 9-6a, the pure water flux of membranes modified at pH 5 was similar to that of unmodified membranes while those modified at alkaline conditions (i.e., pH 8.8 and 11) showed a decrease in pure water flux. Figure 9-6b shows that the membranes modified at pH 5 produced a similar permeate flux to unmodified membranes during oil emulsion fouling while the membranes modified in alkaline conditions showed improved permeate flux during oil emulsion fouling relative to that of unmodified membranes. These results suggest that polydopamine was not successfully coated on the membranes in acidic conditions while the coating proceeded well in alkaline conditions. All modified membranes showed minimal changes in true NaCl rejection from unmodified membranes.

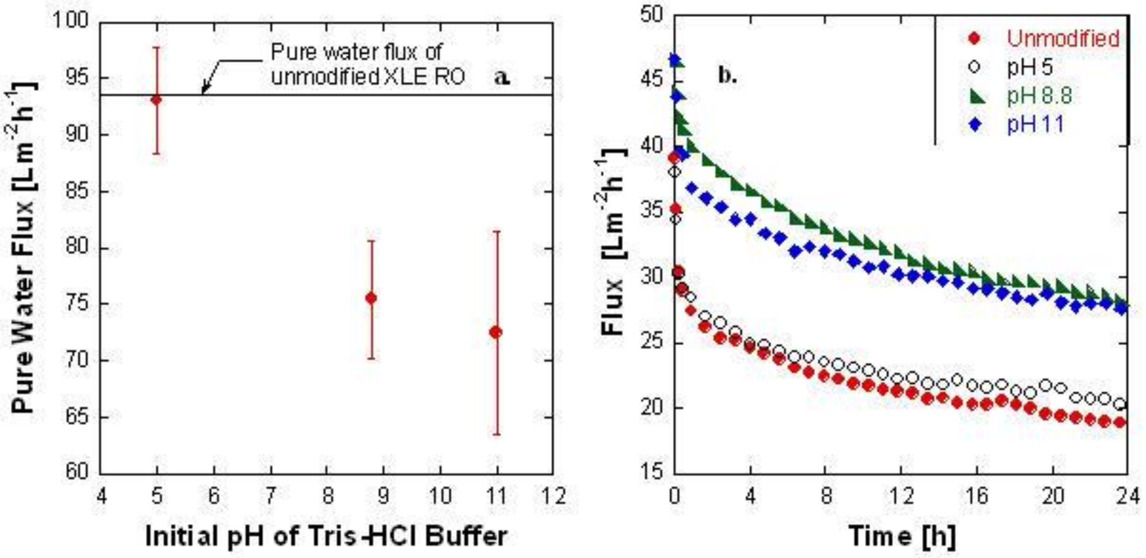


Figure 9-6: a. Pure water flux as a function of Tris-HCl buffer initial pH used during PA XLERO membrane modification, b. Permeate flux as a function of time in soybean oil/water emulsion filtration using PA XLERO membranes unmodified and PDOPA-modified at different initial pH of Tris-HCl buffer (with 2 mg/mL dopamine concentration and 60 minutes deposition time).

Deliverables

Topical Reports

Li, A., S. Kasemset, D.J. Miller, B.D. Freeman, and M.M. Sharma. Innovative UF / NF / RO Membrane Performance Through the Use of Innovative Coatings: Selection of Membrane Supports and Coatings for Barnett Well Flowback Water Separations. RPSEA Report No. 08122-05.03. November 2010.

Lee, A., S. Kasemset, D.J. Miller, B.D. Freeman, and M.M. Sharma. Novel Fouling-Resistant Membranes for Barnett Shale Water Management and Reuse. RPSEA Report No. 08122-05.13. February 2012.

Impact to Producers

Reverse osmosis, ultrafiltration, and nano-filtration are commercially available membrane processes commonly utilized in the water and food industries. The use of these technologies for the treatment of flowback and produced waters requires that they be robust and economical. This project takes a preliminary laboratory-scale investigation of simple (and available) chemical pre-treatment of commercially available membranes to render them more resistant to fouling. Most of the energy consumed in a membrane-based process is the power required for the feed pumps. The ratios of energy used per unit volume of permeate of unmodified membranes and PDOPA-modified membranes were calculated[11] and compared (assuming that the pump efficiency and feed flow rates in both cases were the same). At the same transmembrane pressure difference and based on the flux after 1 hour of oil/water emulsion filtration, the modified PA XLERO membrane could produce 1.26 times more permeate than an unmodified membrane, and the modified PS-20 UF membrane could produce 2.35 times more permeate than an unmodified membrane.

Preliminary test results indicate that the polydopamine coatings developed by UT can be economically implemented to reduce energy costs by more than 35% and extend membrane life by 2-3 fold. Improved membrane technologies can potentially reduce brine demineralization costs to well below $1/bbl. Impact to producers will consist of significantly lower costs for brine volume reductions and significant savings in reduced transportation and disposal expenditures.

Conclusions and Recommendations

Implications: Reverse osmosis, nanofiltration, and ultrafiltration processes are potentially useful technologies for the desalination of flowback waters. The challenge in using membrane technology for produced water purification is fouling. Fouling is the build-up of particulate matter on the membrane either externally or internally which eventually inhibits its activity. Unlike regular seawater or brackish water, produced water contains many particulates, such as emulsified oils and organics, which aggressively foul the membrane. Polydopamine (PDOPA) was found to be an effective anti-fouling surface coating for UF, NF, and RO membranes for produced water purification. The deposition of PDOPA improved the permeate flux for all types of membranes studied during simulated oil/water emulsion filtration. For UF membranes, additional grafting by using poly(ethylene glycol) (PEG) further enhanced the fouling resistance. Energy savings were estimated for the PDOPA-modified UF and RO membranes in oil/water emulsion filtration by comparing power required per permeate volume. With the same amount of energy provided by the pump, the modified RO membrane produced 1.27 times more permeate volume than unmodified RO membrane after 1 hour oil/water emulsion filtration. The modified UF membrane permeate volume increased by a factor of 2.35 after 1 hour of oil/water emulsion filtration. By translating these benefits for industrial membrane applications, PDOPA modification is estimated to provide savings for 30% of the capital and 40-80% of the operating costs.

Outlook: The implementation of reverse osmosis or ultra filtration to the needs of gas and oil industry is under investigation. The present report suggests that this it is highly feasible to produce high quality water for $1-2/ barrel.

Value: The value of this development effort was to define the process capability of a standard and readily available process (reverse osmosis or ultra filtration) to a new application area (flowback water). The data generated in this project are available for industry engineers to peruse and evaluate to make rational process decisions.

Future Considerations: The data in this report were used for membrane selection and preparation for a 30 field test at a flowback water treatment facility in the Barnett. The results of this test are the subject of the next section of this report (Task 10: Field Assessment and Anti-Fouling Polymeric Membrane Coatings for Treatment of Barnett Shale Flowback Produced Water. RPSEA Report No. 08122-05.05. March 2011.

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10 Field Assessment of Anti-Fouling Polymeric Membrane Coatings for Treatment of Barnett Shale Flowback and Produced Waters

Rationale

The purpose of this effort is to test the advanced coated membrane materials in membrane processes treating flowback waters under actual field conditions. This task is a companion effort with Task 9 which was the laboratory development of polymeric (polydopamine) coatings for the improvement of ultrafiltraion and reverse osmosis membranes for the low cost, dependable demineralization of moderate strength flowback and produced waters. Long-term water management in the shale gas industry will depend heavily on water reuse and brine volume reductions to control transportation and disposal costs. Reverse osmosis conceptually works well as a process to dewater moderately concentrated brines before the concentrated brines are introduced to the more capital and energy intensive thermal distillation processing to achieve further brine volume reductions.

Energy efficiency and fouling resistance goals are key metrics in the improvement of membranes using innovative coatings. Efficient water recovery using low cost membrane technology can be used treatment can be achieved using membrane-based processes. A significant challenge to membrane processes tested on produced waters in the past has been membrane fouling. The development of a new generation of ultrafiltration (UF) and reverse osmosis (RO) membranes that could resist fouling, while achieving energy savings relative to conventional thermal treatment, would open opportunities for the use of low-energy-input membrane processes to recover a purified water stream from large volumes of produced water. This task (Task 10) is a field experimental evaluation of advanced membrane coatings developed in Task 9 of this RPSEA project.

Objective

Polydopamine (PDOPA) was found to be an effective anti-fouling surface coating for UF and RO membranes with laboratory simulated flowback waters (Task 9). The deposition of PDOPA improved the permeate flux for all types of membranes. These efforts projected savings of up to 30% of the capital and up to 40-80% of the operating costs. The objective of this task (Task 10) was to determine if these projected savings would translate from the laboratory to field experience. A UF-RO test unit was operated at the Maggie Spain (See Task 7) water reuse facility region near Fort Worth, TX. The feedstock to the UF-RO unit was effluent from the clarifier at this the Maggie Spain.

Goals

1. Upgrade a UF-RO test unit with commercial membranes improved with innovative coatings.
2. Demonstrate improved membrane performance compared to conventional membranes.
3. Identify clean-in-place (CIP) techniques.

Approach

***Advanced Membrane Technology*:** Coating membranes with a thin layer of polydopamine improves their resistance to fouling and provides a versatile starting point for further surface chemical modifications, as needed. Previous laboratory results have shown improved fouling resistance of polydopamine-coated UF and RO membranes (See Task 9) with simulated flowback water.

Field Test: A 30-day field test of a modified UF-RO unit was performed at the Maggie Spain water reuse facility (See Task 7) in the Barnett Shale region near Fort Worth, TX. Feed water to the membrane unit was generated under normal process conditions extant at the Maggie Spain facility, e.g., pH control, coagulation and sedimentation.

Figure 10-1: UF-RO Site at the Maggie Spain Water Reuse Facility

UF-RO Test Unit: The UF system was designed and built by Advanced Hydro Inc. (Figure 10-1). A schematic of the test unit is presented in Figure 10-2. Two hollow-fiber ultrafiltration elements were used: one element was treated with polydopamine and PEG, the second element was not treated (conventional UF membrane) and used as a control. Both elements were run in parallel during the test period. UF effluents were blended in a storage tank (middle buffer tank) that was subsequently fed to the RO system.

Two trains of RO membranes, each with three elements in series, desalinated the water processed by ultrafiltration. Elements in one of the RO trains were treated with polydopamine while the elements in the other train were left uncoated (conventional membrane technology). The two trains of the RO system were run alternately every 12 hours.

An Ultra-Flo U630C (Ultra-Flo PTE Ltd, Singapore) was used as the demonstration UF membrane module. The membrane fibers were modified poly(acrylonitrile) with a 1mm outer diameter (pressure side) and a 0.5 mm inner diameter (Filtrate side). The membrane surface area in each module was 323 ft^2. Pore sizes reportedly ranged between 0.1 to 0.01 microns. The membranes were available off-the-shelf and typically used for water treatment with a recommended maximum feed turbidity of less than 5 NTU. Such membranes are not optimum for produced water pre-treatment; however, these were the only membranes available for the side-by-side testing.

A spiral-wound SWC3+ seawater RO membrane module (Hydranautics, Oceanside, California, USA) was used as the demonstration RO membrane. This membrane is a typical interfacial composite polyamide RO membrane with a nominal surface area of 400 ft^2 per membrane module.

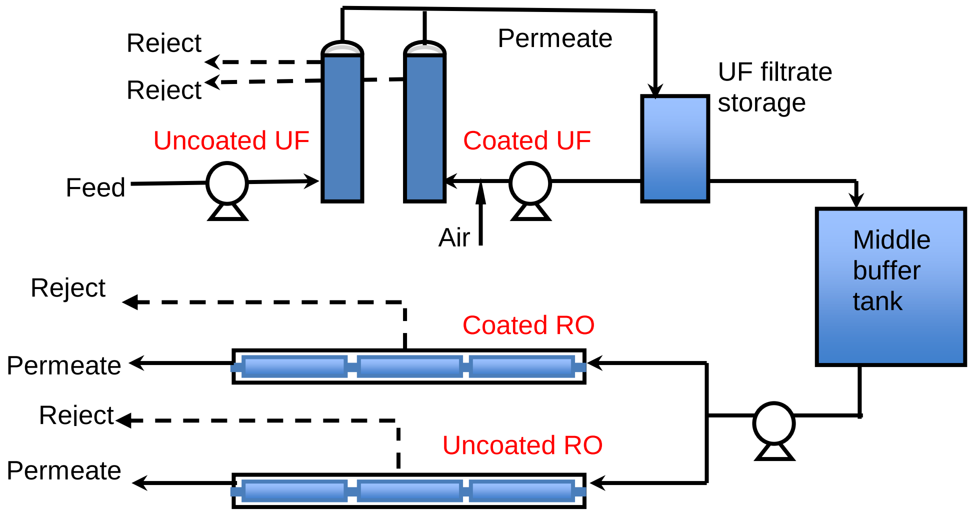


Figure 10-2: Pilot test schematic showing UF and RO systems

Clean-in-Place: Due to the high fouling potential of the feed water, hollow fiber modules were back-flushed every 15 minutes with a 30-second air scour. To maintain the membrane performance, a daily hot water clean (110°F) was also performed on hollow fiber modules at the beginning or end of each day's operation. Fully automated real-time flow and pressure data were recorded every minute.

Two types of membrane cleaning methods were employed to recover UF membrane performance: chemical-enhanced hot water clean (HWC) and standard chemical clean-in-place (CIP). RO permeate was used for the daily HWC. The membrane elements were first flushed with RO permeate. Heated (125 °F) caustic (pH 11) or citric acid (pH 2) solutions were circulated through the membranes for 30 minutes. After the HWC, membrane modules were flushed again with RO permeate. CIP was occasionally performed on ultrafiltration membranes as a more intensive cleaning procedure. During CIP cleaning, caustic cleaning with NaOH (1 wt.%) was performed first for 2 hours and followed with citric acid (2 wt.%) cleaning for 1.5 hours. Cleaning solutions were also maintained at 125°F during circulation. The membranes were fully flushed with RO permeate.

Performance Evaluation

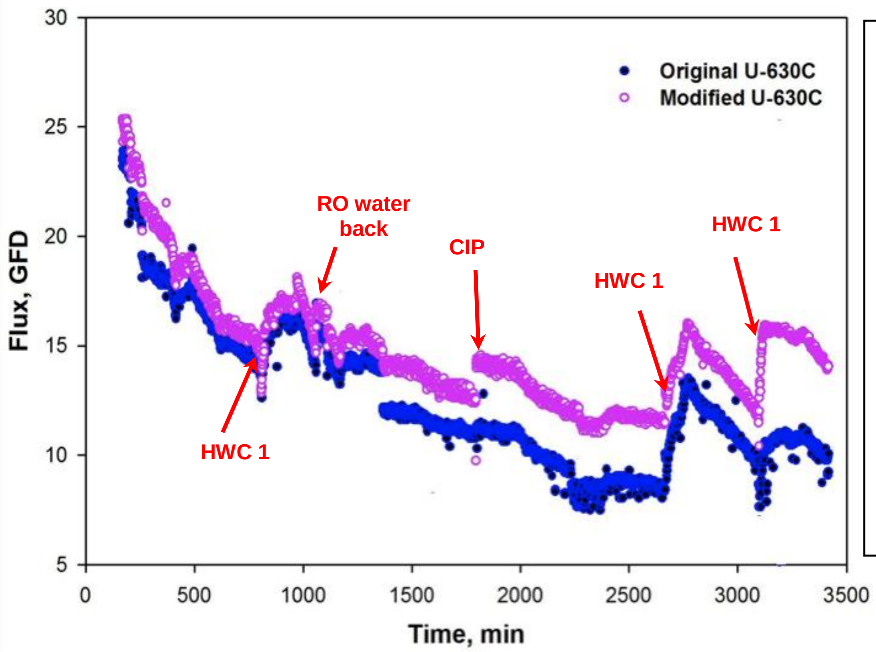
Ultrafiltration membrane efficacy was evaluated by monitoring membrane permeate flux, applied transmembrane pressure difference, and cleaning frequency. These data and parameters were recorded during the filtration operation. Coated membrane performances were tracked and compared with that of the non-coated controls.

Reverse osmosis membrane performance was characterized based on salt rejection and permeate flux. Overall productivity was also evaluated in terms of recovery and net driving pressure.

Results

Ultrafiltration: Hollow fiber UF membranes were tested in parallel to compare polydopamine/PEG-coated and uncoated (conventional) elements. All operating conditions and cleaning procedures were identical for both elements. During the approximately 60 hour run, coated membranes demonstrated significantly better performance than uncoated membranes. Coated elements generated more permeate (i.e., higher flux) than uncoated elements. This advantage in water productivity became more significant during the latter stages of the run, as the membranes fouled.

Figure 10-3 presents the permeate water flux from the UF elements during the performance period. Pilot testing began with new membranes with the initial flux for both hollow fiber modules set at 25 gallons per square foot of membrane per day (GFD) (i.e., 42.4 liters/(m^2 hr) (LMH)). Flux of both membranes decreased gradually over time. Although both coated and uncoated control membranes experienced flux decline during the 60 hours of pilot operation, coated membrane provided nearly 50% higher flux than the uncoated control membranes. Irreversible losses from 25 to 15 GFD are due to the fact that membrane module is not optimal for high-turbidity water and had a very tight fiber geometry to achieve higher surface area.



HWC1: caustic enhanced hot water clean, pH=11, 30 minutes circulation at 110 °F.

CIP: clean-in-place, with caustic clean first, pH=11, 2 hours circulation at 110 °F; followed with citric acid clean, pH=2, 1.5 hours circulation at 110 °F.

RO water back flush: UF membranes were flushed using demineralized water from the RO process.

Figure 10-3: Water Flux on the UF Filters: Coated versus Conventional Membranes

During the operation, chemical cleaning was performed on both elements at the intervals shown in Figure 10-3. Caustic-enhanced hot water cleaning (HWC 1 in Figure 10-3) was found to be effective to recover flux. During the final days of test period, the coated membrane produced approximately 50% more water than the uncoated control. In addition, HWC and CIP cleaning appeared to be more effective for the coated membrane than for the conventional membrane. The typical flux for the coated membrane was maintained at 12-16 GFD using only daily caustic-enhanced HWC. The typical flux for the uncoated UF membrane was maintained at between 7-11 GFD.

Trans-membrane pressure difference (TMP) is a measure of the pressure difference across the feed and permeate sides of the membrane during the filtration process. When a fouling layer is present, the membrane becomes less permeable, leading to an increase in TMP. TMP was measured for both coated and uncoated membranes (Figure 10-4). The uncoated membrane consistently showed ~25% higher TMP than the coated membrane. The typical differences are on the order of 4-5 psi.

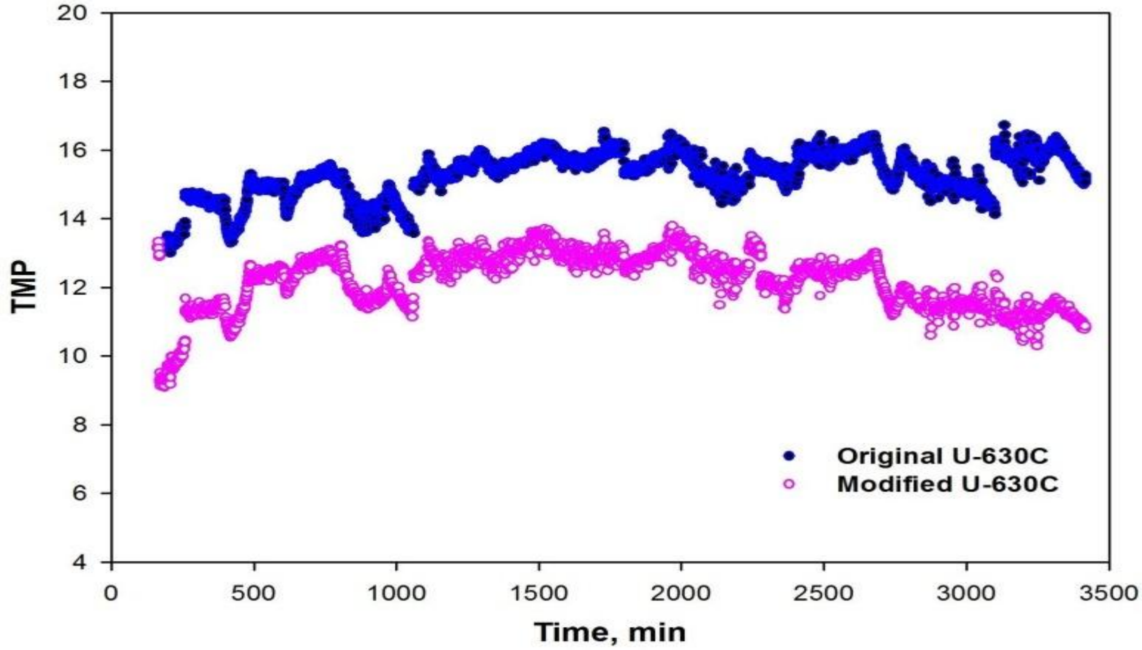


Figure 10-4: Trans-membrane pressure (TMP) data for two side-by-side UF

Despite nearly 25% lower TMP across the coated membrane, this membrane was generating about 40-50% higher flux during the second half of the pilot (post initial fouling). The ratio of flux to TMP, called the specific flux (GFD/psi), is presented in Figure 10-5. These data represent a direct measurement of productivity of the filtration process relative to its energy consumption. Notably, higher specific flux is obtained for the coated membrane. The coated membrane operated at about 1.5 GFD/psi compared to the uncoated membrane at 0.8 GFD/psi.

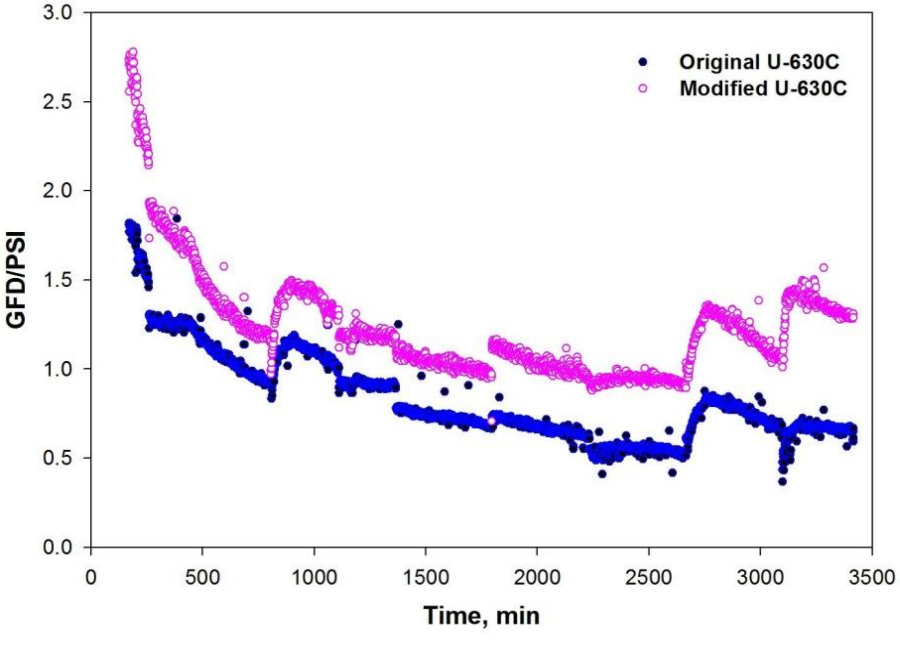


Figure 10-5: Specific flux data for two side-by-side UF hollow-fiber elements

Reverse Osmosis: Permeate from the ultrafiltration membranes was collected in a common tank and supplied to the RO membrane modules as feed for subsequent removal of dissolved minerals (desalination). The feed flow rate was fixed at 15 GPM with an initial recovery at 50%. Antiscalant Flocon 260 was added to the feed line to prevent scaling in the concentrate side of the RO elements. Total dissolved solids (TDS) values, a measure of the mineral concentration of the feed, fluctuated greatly from day to day. The highest measured value for TDS reached about 63,000 mg/L. Since the RO feed pump was limited to 1000 PSI, recovery could only be maintained at 10-15% due to the high salinity of the feed. Specific permeate flux and rejection were normalized to 25^{o}C and presented in Figure 10-6 and Figure 10-7.

As seen in Figure 10-6, no significant specific permeate flux advantage was observed for the coated SWC3+ membranes relative to the uncoated membrane. The normalized specific flux data show significant random variations for later half of the pilot when feed TDS was more than 50,000 mg/L. This may appear unusual; however, such behavior is generally attributed to significant drop of net driving pressure across the RO membrane resulting from significantly increased TDS values.

Coated membranes showed improved and more stable salt rejection than uncoated membranes during the entire pilot (Figure 10-7). The uncoated membranes experienced a significant decrease in rejection when the feed TDS increased. Rejection of uncoated membranes started at 99.5% and dropped to a lowest value of 96.6%. However, for coated membranes, rejection was maintained above 99.5% throughout the pilot.

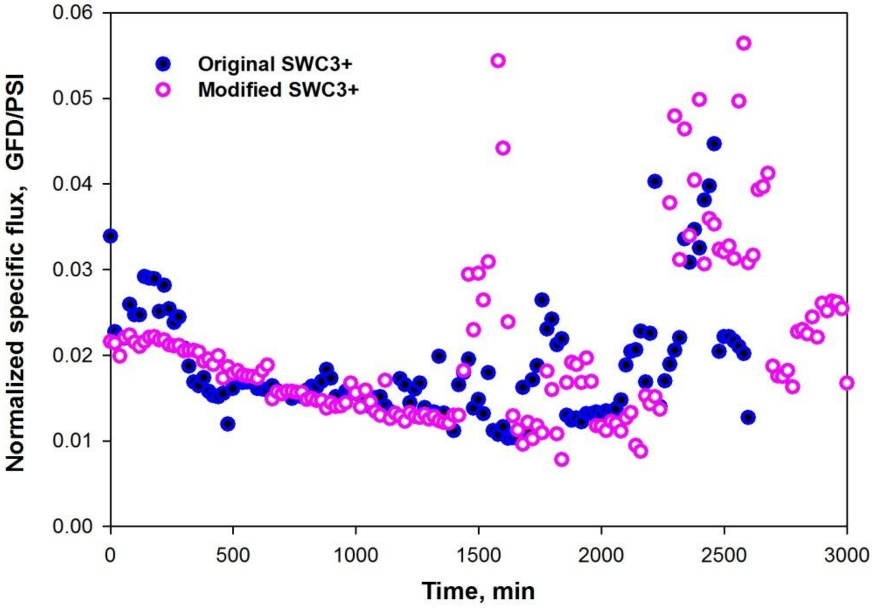


Figure 10-6: Specific flux data for two side-by-side RO hollow-fiber elements

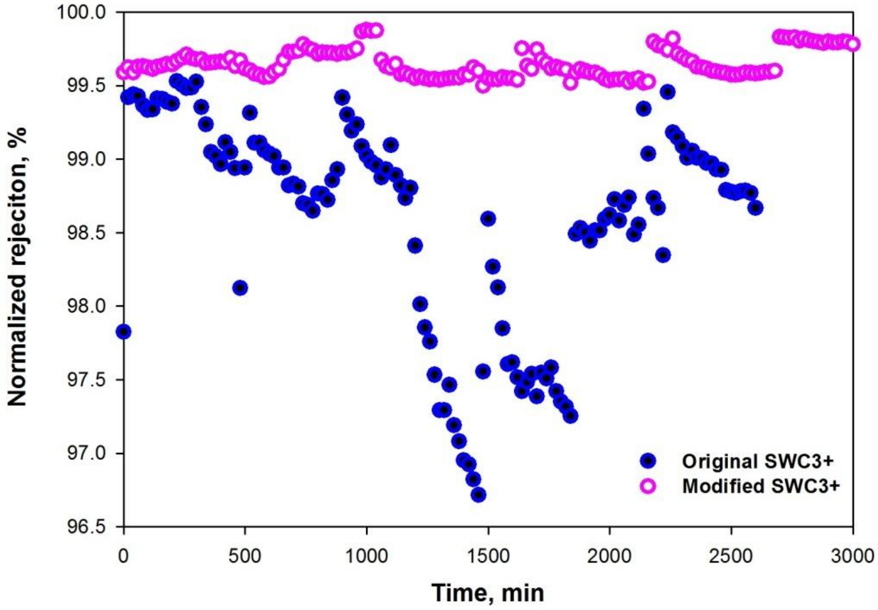


Figure 10-7: Normalized TDS Rejection, Coated and Non-Coated RO Membranes

Chloride and hardness (Ca2+, Mg2+) concentrations were measured using on-site titration for feed and permeate RO water to evaluate the individual rejection of specific ions. Results are presented in Table 10-1. Rejection of chloride and hardness ions was higher for the coated membrane than for the uncoated membrane. This observation is also in agreement with the rejection data presented in Figure 10.7, which was evaluated using on-line conductivity measurement.

Table 10-1: Specific Ion Rejection of Coated and Uncoated RO Membranes

	Coated SWC3+			**Uncoated SWC3+**		
	Feed	**Permeate**	**Rej$_{ave}$**	**Feed**	**Permeate**	**Rej$_{ave}$**
Cl-, mg/l	39000	190	99.80%	35750	666	98.30%
	36500	122		31000	448	
	35000	75		35500	625	
				31650	650	
Total Hardness,mg/l (as $CaCO_3$)	12000	12	99.90%	10000	185	98.40%
	10200	10		8800	106	
	10000	6		10000	170	
				9200	124	
Ca^{2+},mg/l (as $CaCO_3$)	10500	11	99.90%	8900	160	98.40%
	9000	5		6600	95	
	8900	2		8500	147	
				7400	108	
Mg^{2+},mg/l (as $CaCO_3$)	1500	1	99.70%	1100	25	98.70%
	1200	5		2200	11	
	1100	4		1500	23	
				1800	16	

Deliverables

Topical Reports

Shiner, S., R. Hayes, D. Agnihotri, R. Li, X. Huang, P. Sirirat, and A. Li. Membrane Fouling Reduction Test Plan – Processing Shale Gas Flowback and Produced Water. RPSEA Report No. 08122-05.02. December 2010.

Huang, X., Agnihotri,D., Freeman, B.D., Hayes, R., Kasemset, S., Lee, A., Li, H., Sharma, M., and Shiner, S., Field Assessment and Anti-Fouling Polymeric Membrane Coatings for Treatment of Barnett Shale Flowback Produced Water. RPSEA Report No. 08122-05.05. March 2011.

Completed Manuscript to be Submitted to Journal of Membrane Science in 2012

Miller, D.J., X. Huang, H. Li, S. Kasemset, A. Lee, D. Agnihotri, T. Hayes, D.R. Paul, and B.D. Freeman. Anti-Fouling Membranes for the Treatment of Flowback Water from Hydraulic Shale Fracturing: A Pilot Study. (2012).

Impact to Producers

The objective of this project was to determine if the previously discovered advantages (Task 9) of antifouling coatings applied to UF and RO membranes would translate in the field. These results demonstrated that, indeed, antifouling membranes show improved performance over their uncoated counterparts without any loss of flux. Coated hollow fiber UF membranes gave about 50-100% more water productivity than the uncoated ones. Cleaning operations were more efficient in recovering flux and pressure for the coated membranes. Coated seawater RO membranes achieved better salt rejection than uncoated membranes. Under the circumstances of very high salt concentrations, uncoated SWC3+ membranes experienced significant decline in salt rejection, while coated SWC3+ membranes maintained salt rejection values above 99.5%. No noticeable flux decrease was observed on either coated or uncoated RO membranes.

Conclusions and Recommendations

Operation of the field-based experimental test skid that employed commercial scale membrane modules to provide a side-by-side comparison of performance of coated and un-coated ultrafiltration (UF) and reverse osmosis (RO) membranes in the treatment of actual flowback waters was successfully completed over a 30 day period. Conclusions from the limited field trials are the following:

1. Polydopamine was successfully applied to modify commercial-sized ultrafiltration and reverse osmosis membrane modules. Ultrafiltration modules were further modified by grafting PEG to the polydopamine coating. Modified and unmodified modules were employed in a pilot-scale study for several days where they were challenged with flowback water from hydraulic fracturing operations in the Barnett shale gas basin.
2. Modified UF membranes showed improved flux and decreased transmembrane pressure and, consequently, higher specific flux than their unmodified counterparts over the entire study. Further, both modified and unmodified UF modules were cleaned regularly with typical chemical cleaning regimens; the modified UF module showed enhanced flux recovery after cleaning.
3. The polydopamine-coated RO membranes did not show enhanced flux or depressed transmembrane pressure relative to the unmodified module. Following pretreatment with UF, the flowback water stream had very low levels of oils and greases and suspended solids that challenge RO membrane operation. Longer field trials are needed to demonstrate the long term reduction in pressure drop requirements that were observed in the lab with the corresponding RO membrane treatment units.
4. Salt rejection, however, was both higher and more stable in the coated RO membrane modules than in unmodified modules, presumably due to caulking of minor defects in the thin polyamide separation layer. Previous work on polydopamine membrane coatings has focused on laboratory-scale filtrations; this study demonstrated that polydopamine and PEG can be employed in the modification of industrial membrane modules and improved the fouling behavior of those modules when challenged with complex, highly-fouling feedwater. Polydopamine and polydopamine-*g*-PEG modifications can improve the quantity and quality of permeate from membrane-based industrial water purification.

Implications

The major implications of this development effort relate to the process needs and changes required to meet the aggressive water chemistry in flowback waters.

- UF-RO systems appear to be an alternative treatment process for early flowback waters, with only minimal pretreatment (coagulation and settling) required.

- These systems can be improved, in both rate and robustness, by the application of antifouling coatings to the membranes.
- The antifouling coatings represent a simple chemistry applied to readily applicable to commercially available membranes.
- The advanced coatings maintained activity (at least) during the 30 day test period.
- Standard clean-in-place technology was sufficient to maintain the process advantage imparted by the advanced coatings.

Value The polydopamine coating technology evaluated in the field during this effort has considerable value in reducing energy costs and extending membrane life in UF-RO treatment systems. UF-RO is a standardized, commercially available process. Advanced Hydro is working on the development of a service to provide enhancement coatings to UF and RO membrane modules in the field through "in-situ" coating applications. This project shows the industry a pathway to apply, maintain, and improve membrane processes specifically for the treatment of flowback waters.

Outlook and Future Considerations With successful demonstration of the Ultra and Micro filtration with Polydopamine coating and PEG coatings along with salt rejection improvements on RO membranes, Advance Hydro Inc. actively pursued commercialization efforts since beginning of 2011. During a period of one year, significant progress toward the commercialization of this technology included the following milestones –

1. Advanced Hydro Inc. (AHI) and Geopure Hydro Technologies (GHT) formed an exclusive partnership to market a turn-key solution for reuse of Frac and produced water in the E&P space.
2. As part of the agreement, AHI will provide a complete solution that includes coated MF/UF membranes along with additional technology component such as TSS removal, softening, UF/MF as well as RO.
3. GHT is now offering AHI's turn-key solution to their potential customers. This solution is based on a service based model where customer can treat their water on a $/BBL basis.
4. In parallel with a turn-key solution, AHI also validated an additional polymer technology to remove light petroleum hydrocarbons that are abundantly and commonly found in the Frac and Produced water as TOC. A significant R&D effort was put in place to evaluate polymers that have capability to replace activated carbon, resulting in a pilot scale skid development.
5. Additional pilot testing of AHI's turn-key solution was recently completed in Dallas Fort Worth during Feb. 2012. Three major E&P companies attended the batch-scale simulation and piloting of our turn-key continuous treatment process.
6. A fully automated, commercial scale (250 gallons per minute, >5000 BBL/day) system is currently under integration. This system will be available for product-scale evaluation for

a customer in Texas during this summer. Permit application for this treatment system has been in process with TCEQ/Texas Railroad Commission.

7. The treatment solution is now available as a commercial product (5000 BBL/day system) including a TSS removal process, followed by softening process, followed by polishing based on coated MF/UF technology. The final stream can be desalinated using RO or reused as it is for Hydraulic Fracturing.
8. Designs are in progress for a 2-3x longer membrane cycle-life with the coatings technology for use with these challenging waters. In addition, other technologies for removal of light hydrocarbon targeted.
9. A series of several field pilots (250 BBL/day) with continuous process stream are planned during March – May 2012 followed by demonstration of a commercial scale system.

11 Systems and Life Cycle Analysis

Rationale

Water management issues within a multiple-well, multiple-field gas play are time dependent. The time-frame for comprehensive water management may span several decades; from the drilling of the first well; to the completion of the first field; to the integration of multiple fields within the play; to the closure of the last well. Different problems arise, and different solutions need to be developed at every phase of the life-cycle of the play. This task describes a first look at the water and waste management issues spanning a 45 year development period based on a projected 4800 well play. The results of a computer model, based on a hypothetical play within the Marcellus, suggest that there are three distinct management periods; young play, middle-age, and old-aged play.

Objectives

The objective of Task 11 was to investigate the known database of single well flowback events, and to project these results throughout a 45 year life-cycle of a multiple field play. Key problems addressed included projected flowback and produced water generation, salt concentration and salt mass generation, truck traffic, drilling spoil production, disposal and landfill costs, and transportation and carbon footprint costs.

Goals

As the project developed, the specific goals were refined and refocused to develop a general engineering analysis and supporting computer model sufficient to identify the broad management issues facing the development of a gas play. Specific issues were identified and sensitivity tests were run to present a rational projection as to the criticality of these issues (see Hayes and Severin – RPSEA Report No. 08122-05.10). The generic goals and summary findings are presented below.

1. Determine baseline operation in the development of a single wellhead.
2. Determine a sequence of operations typical for the development of a multiple well field with accommodation for multiple re-fractures at each well.
3. Determine a sequence expected for the development of multiple well fields within a play.
4. Integrate goals 1–3 into a rationale suitable for computer projection.
5. Identify key operational and situational parameters, and determining the sensitivity of these parameters on overall life of the play.
6. Integrate these projections with rational costs estimates.

Approach

The initial flowback rates and salt concentrations from series of tests from the Barnett and the Marcellus were analyzed (See Hayes and Severin – RPSEA Report 08122-05.09, 2012; and, Hayes and Severin – RPSEA Report 08122-05.10, 2012). Figure 11-1 shows the anticipated flowback recovery rate and recovered flowback volume as a function of pumping days past fracture for the median Marcellus event. Figure 11-2 gives the projections for the wellhead concentration, impoundment concentration, and total salt recovered as a function of the recovered flowback volumes for the anticipated median Marcellus flowback event.

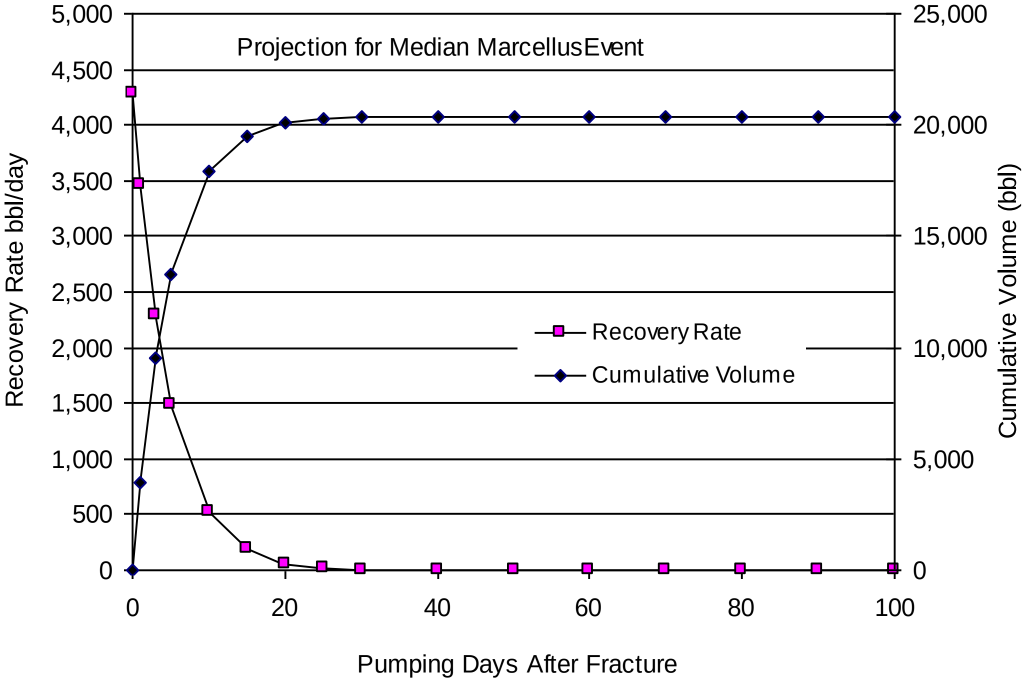


Figure 11-1: Anticipated Flowback Recovery Rates and Cumulative Volumes for a Single Well Calculated with the Median Marcellus Parameters

A computer model was written in Microsoft Excel Visual Basic. The concept behind the model was to establish the relative dates for initiation, completion, refracture(s), and closure for a single well. The results for a single well were then reproduced for all wells in a field based on the initiation date of each individual well. The results for the entire play were then reproduced by duplicating the dates for the field, offset as dictated by a number of operational variables. The result is a compilation of the significant dates for up to 32 wells per field at 500 fields per play on a daily basis for up to 45 years. The variables in the model are presented in Table 11-1. The parameters in Table 11-1 represent the simulation used for the Median Marcellus event with an estimated long term water recovery of 7 barrels/day (produced water). The base case assumed initial fracture plus three additional refractures during the life of each well.

Results and Discussion

Observations on the Base Case: The base case (Table 11-1) is 16 wells per field and 300 fields per play for a total of 4800 wells. With a drilling rate of 25 days per well and an installation delay of 7 days between wells, the first field takes about 1.5 years to complete. The final refracture in the first field is completed by year 10 (Figure 11-3).

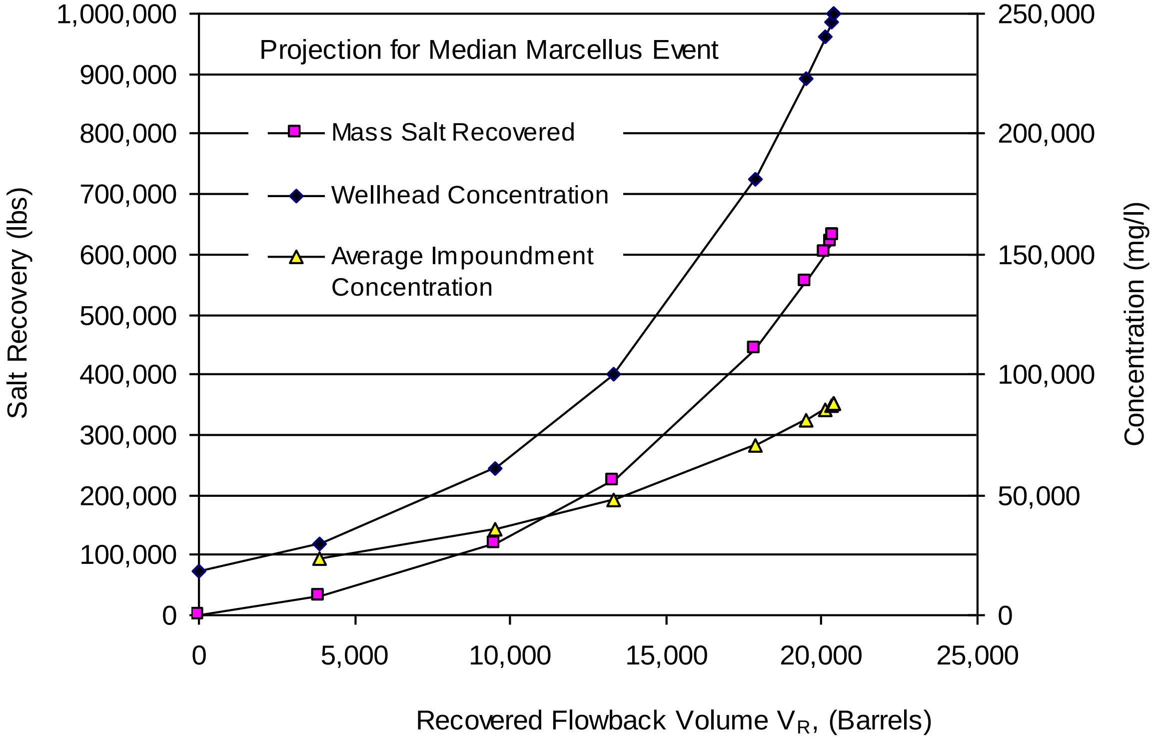


Figure 11-2: Anticipated Wellhead Concentration, Impoundment Concentration, and Total Salt Recovered as a Function of Recovered Volume, Calculated as the Median Marcellus Event.

Table 11-1: Parameters Used in Most Model Analyses (Base Case)

Define the duration of play in years	45 years
Closure (days after final refracture)	8000 days (29.1 years)
Number of wells in a field	16
Number of fields in development	300 (48% coverage)
Total Projected wells in play	4,800 wells
Concentration of the produced water ppm	250,000 mg/l
Number of refractures expected	3
Days to install a single well	25 days
Days between install and next well start	7 days
Days to mobilize to new field	3 days
Days between completion and refracture	1,000 days
Produced water bbl/day	7 barrels
Number of driller teams	12
Spent Drilling Mud Recovered per well	53 tons per well
Rock Cuttings per well drilled	873 tons per well

Many drilling companies plan to reuse much of the flowback water for drilling the subsequent well. Since within a single well field, numerous completions and re-fractures are conducted over the construction and operation of the field, the observed daily output of brines from the well group can vary considerably. Each of the 16 wells are completed on separate days; each of these wells are re-fractured on separate days separated by weeks of time. This leads to a highly varied output of brine from each wellfield as shown in Figure 11-3. This wide daily variability of the flow rate and quality of the flowback water will impact the choice of on-site pretreatment processes (such as suspended solids, iron control, and other quality issues) needed to process the flowback for reuse.

The end of easy on-site reuse begins at the completion of the final well on or about 1.5 years. Water generated past 1.5 years at this field becomes more and more concentrated based on the assumptions for the processed water (7 barrels per day per well). Ultimately about 100 bbl/day of concentrated brine is generated as produced water from the field. Under certain conditions, refracturing is applied to wells to improve natural gas production rates in later years. The model allows for three or more refractures planned for each well during the life of the play. It is obvious from this figure that provisions must be made at the field level to accommodate the capture of a very wide range of flows throughout the life of the well field.

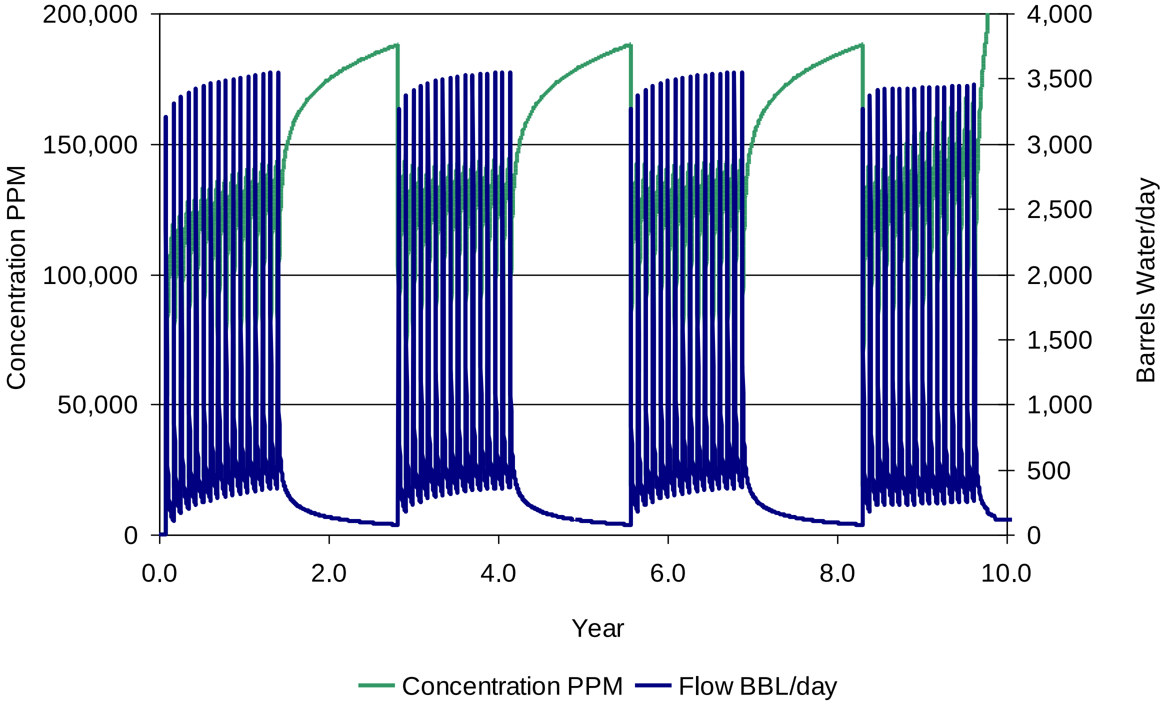


Figure 11-3: Planned Initial Fracture and Three Refractures One Field of 16 Wells (1000 Days Between Fractures)

Long term water management becomes even more complex when the life-time of the play is considered. Some planners are considering the creation of up to 300 fields, each with 16 wells, for a 25 mile x 25 mile area, with upwards of 50% cover of the play. The model was used to define event dates for the activity needed to support 4800 wells. The assumptions in Table 11-1 concerning the mobilization of up to twelve drilling teams were used to generate a table of fracture events. Based on these assumptions, fracture activity occurs for up to 21 years. The water management plan for the play needs to incorporate 19,200 fractures with control of flowback and produced water recovery from each of the 4800 wells (Table 11-2).

Table 11-2: Model Assumptions of Initial Completions And Refractures in a Hypothetical 4800-Well Play Containing 300 Fields, Each with 16 Wells

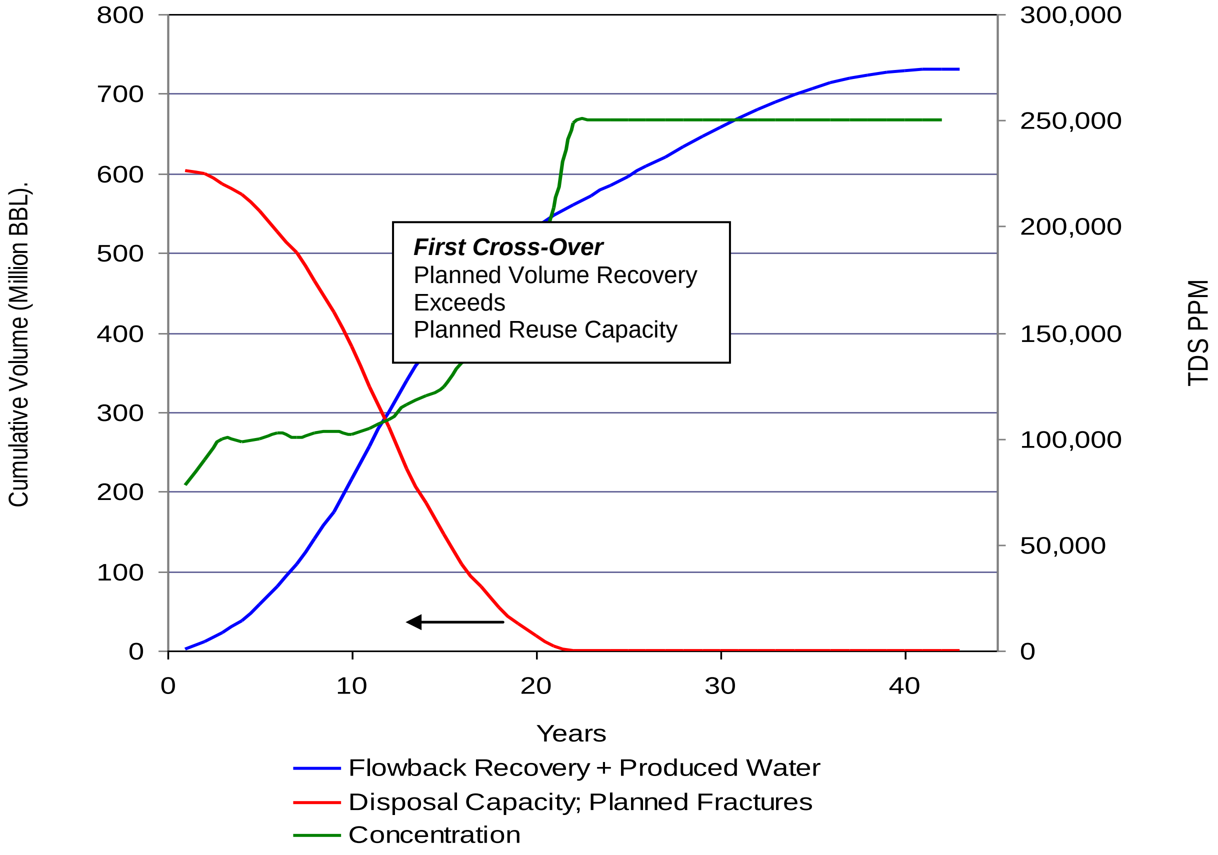
Year	Initial Drilling	Refracture Events	Total Fractures	Year	Initial Drilling	Refracture Events	Total Fractures
1	141	0	141	16	0	904	904
2	391	0	391	17	0	832	832
3	416	8	424	18	0	690	690
4	419	220	639	19	0	441	441
5	416	412	828	20	0	409	409
6	418	455	873	21	0	193	193
7	416	711	1127	22	0	4	4
8	419	836	1255	23	0	0	0
9	416	917	1333	24	0	0	0
10	418	1193	1611	25	0	0	0
11	416	1248	1664				
12	385	1255	1640				
13	129	1248	1377				
14	0	1255	1255				
15	0	1169	1169				

The Marcellus area has some unique water management issues, namely the dearth of deep-well injection resources for final disposal of flowback and produced water. Most non-reuse water is presently trucked to sites in central Ohio. A current practice in the Marcellus is to use as much of the recovered flowback water, as possible, as part of the feed water for the next fracture.

A common fracture event requires about 4 million gallons, or about 95,000 barrels of water. A typical recovery of flowback water is 1 million gallons, or about 24,000 barrels. Each subsequent fracture would require 3 million gallons fresh water plus the 1 million gallons collected from the previous fracture. Therefore, if 19,200 fractures are planned in a 300 field play, then each fractures represents 25% of 4 million gallons, for a total planned reuse capacity of 19,200 x 24,000 = 461,000,000 barrels of reuse capacity. As each fracture occurs, the reuse capacity of that fracture is used-up. It is a matter of book-keeping to compare the total planned reuse capacity of 19,200 fractures versus the total of the flowback water plus produced water collected.

Figure 11-4 is an example of a 19,200 fracture Marcellus play assuming that an even larger percent reuse (33%) than described above is assigned to each fracture. The red line represents the planned reuse capacity. The blue represents the recovered flowback plus produced water. The green line represents the average concentration of the recovered water. *The planned capacity curve crosses the recovered water curve at about 11.5 years into the life of the play. For reference, this will be termed the* ***first cross-over*** *point.*

The first cross-over point demarks the transition between a young play and a middle-aged play. In the years up to the cross-over, the axiom holds that “all the recovered water can be sent back down-hole”. At year 11.5, however, there remains less reuse capacity available than the projected future recovery. At year 11.5 it becomes difficult to schedule enough reuse to keep up with the recovery.



First Cross-Over
Planned Volume Recovery
Exceeds
Planned Reuse Capacity

Figure 11-4: Cumulative Fracture and Process Water Recovery vs Projected Reuse Capacity in a 19,200 Fracture Play Assuming 33% Blend of Recovered Water in Each Fracture

Figure 11-5 shows the rate of total water recovery versus the rate of reuse capacity. Once again, a generous ratio of 33% blend of recovered water to total water use in the fracture is assumed. The red curve represents the rate of creation of reuse capacity and essentially mimics the rate of fracture events. The blue curve represents the rate of collection of flowback water and produced water. The green line is a reference line for the concentration of the collected water. The plum colored curve is the rate of necessity for non-reuse options. The rate of depletion of reuse capacity (red curve) crosses the rate of flowback generation (blue curve) at about year 15.5 into the life of the play. *This cross-over, termed the* ***second cross-over****, represents the critical point in the life of the play where the rate of generation of flowback and produced water exceeds the production of reuse options.* The life of the play has crossed from middle-age, where water management was difficult, to old-age, where water management is impossible without intervention.

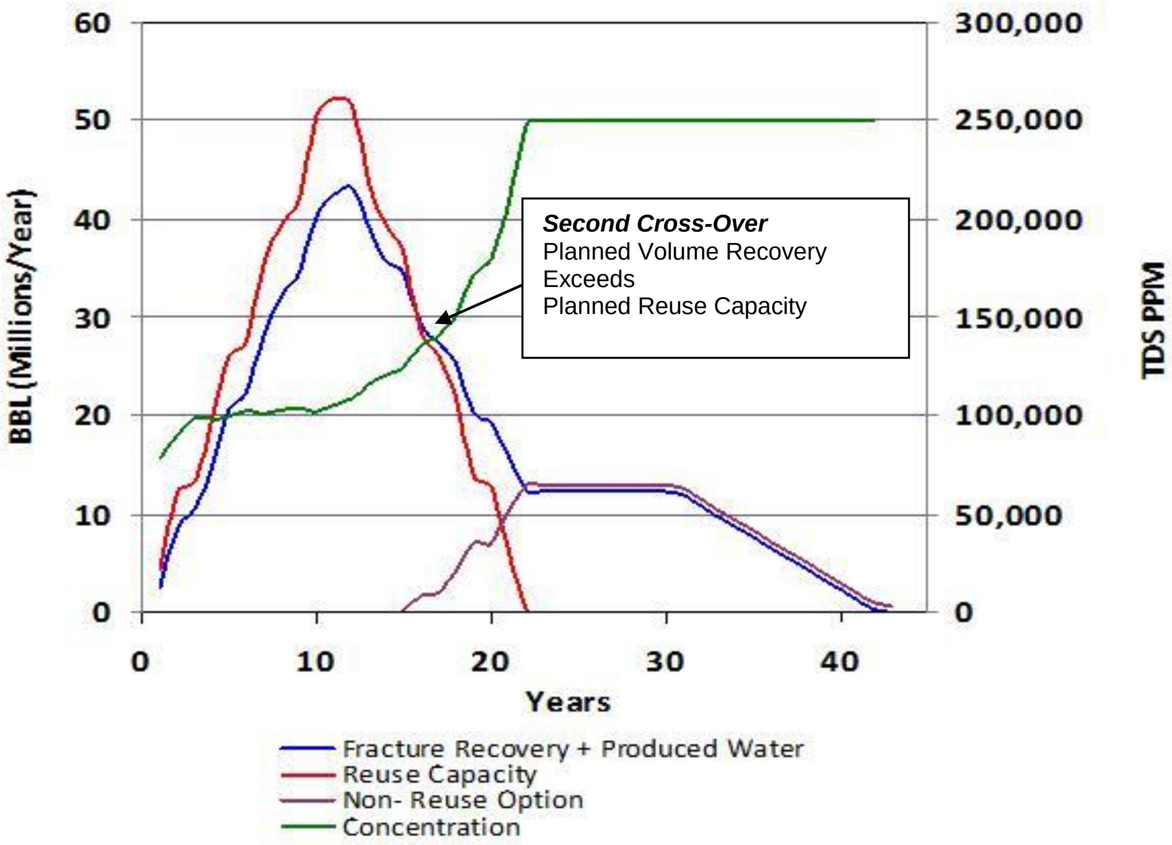


Figure 11-5: Comparison of the Rate of Fracture and Process Water Recovery vs Rate of Reuse Capacity in a 19,200 Fracture Play Assuming 33% Blend of Recovered Water in Each Fracture

Sensitivity Analysis: Number of Refractures per Well: One operational strategy to improve the efficiency of gas production is to hydraulically refracture the well several times throughout its life. Figure 11-6 is a sensitivity analysis using the assumptions of Table 11-1, with the only variable being the number of planned hydraulic refractures per well, ranging from 0 to 4. While planning fewer refractures per well diminishes the magnitude of the water management problem, it does not change the premise that the play will pass from young, to middle-age to old-age. In fact, planning fewer refractures per well causes the onset of middle-age and old-age to accelerate. Paradoxically, the development of the play is dependent upon continued refracture. The place to put recovered water (flowback and produced water) is in the next fracture. The larger the number of fractures planned, the easier it is to reuse the produced water.

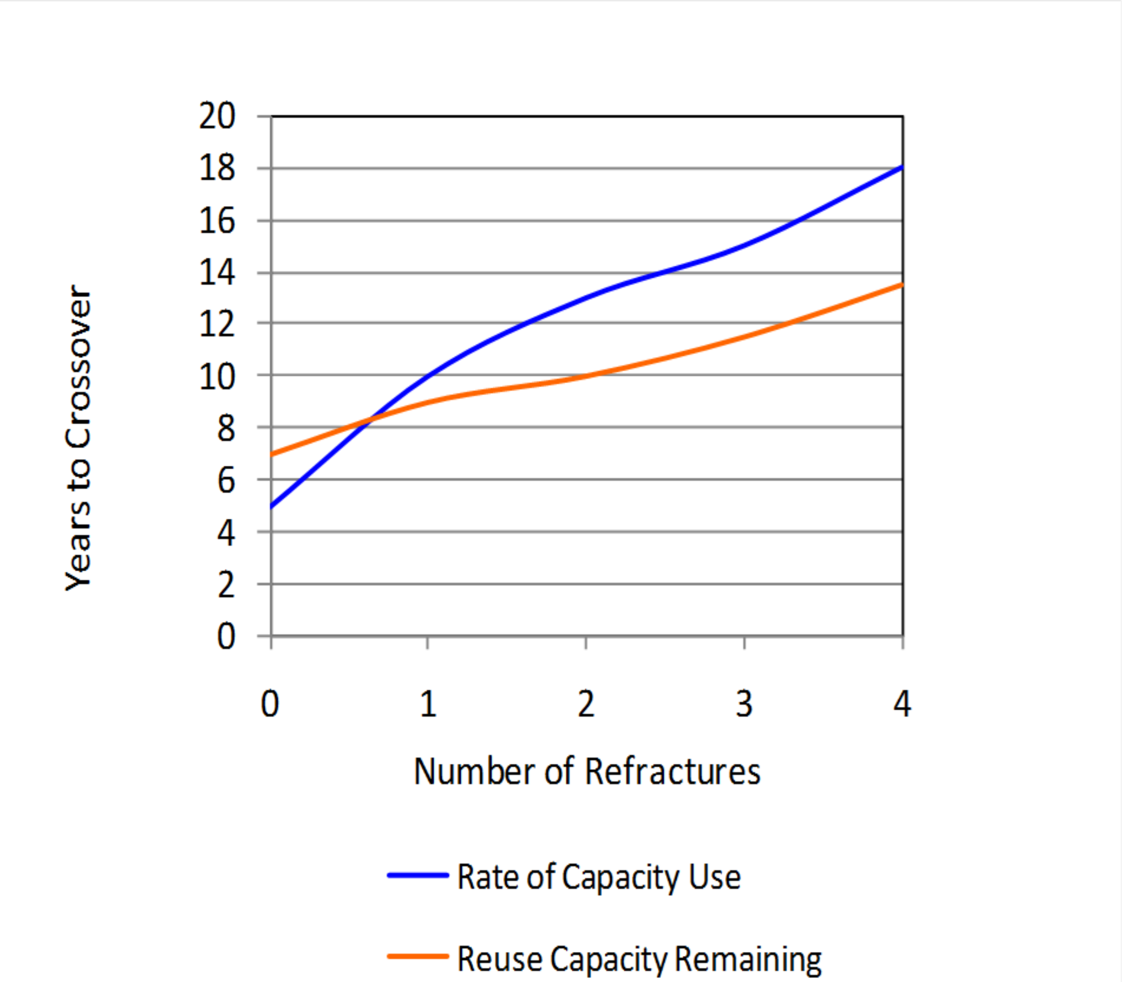


Figure 11-6: Sensitivity Analysis; Onset of Cross-Over Points Based on the Number of Planned Refractures per Well

Sensitivity: Water Reuse Blend Ratio: In the base case the assumption is made that recovered water (flowback and produced water) may be blended with fresh water to formulate the hydraulic fluid for the subsequent fracture. The base case assumes a 33% reuse ratio, i.e., 100,000 barrels of fracture fluid may be prepared with 33,000 barrels of recovered water blended with 67,000 barrels of fresh water. This is an aggressive assumption, as current field practice is a reuse ratio of about 25%. Figure 11-7 is a sensitivity analysis based on the ability to reuse water in a subsequent fracture. The point of this plot is that even if 100% of the total water used for fracture could be recycled water, there will come a point in the life cycle of the play were there is more water collected than can be reused. Essentially, produced water is recovered but no more fractures are planned. The play passes from middle-age to old-age, regardless of the ability to reuse captured water. Increasing the reuse blend ratio delays the inevitable.

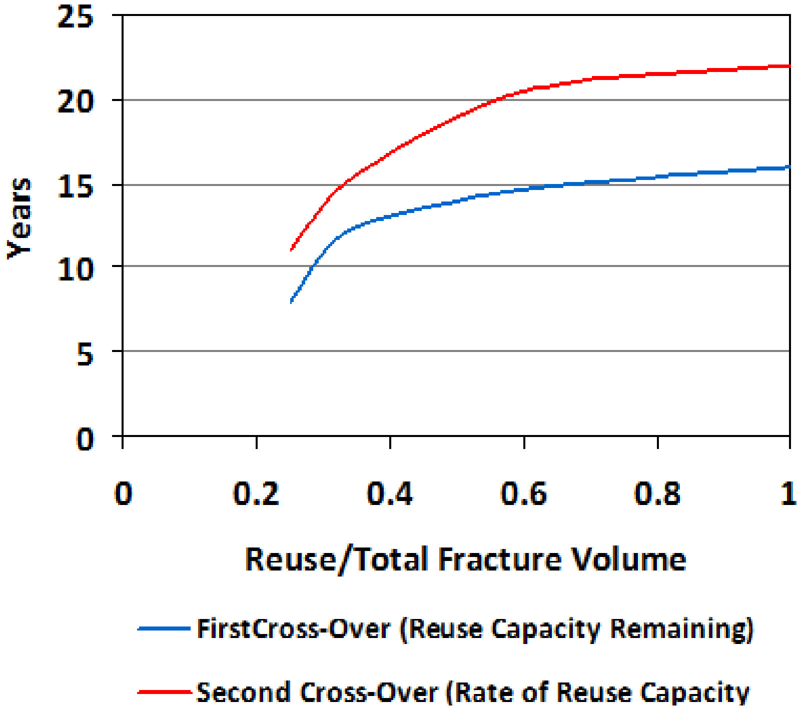


Figure 11-7: Sensitivity Analysis: Onset of Cross-Over Points Based on the Ability to Reuse Recovered Water in the Next Fracture

Sensitivity: Rate of Produced Water Recovery: The generation rate of produced water is a variable in the model. In the base case, this is set at 7 barrels per day per well and a concentration of 250,000 ml/l TDS. Figure 11-8 shows the cross-over years as a function of produced water flow. The grace period leading to the point where the rate water recovery exceeds the rate of reuse capacity generation is about 21 years if the produced water flow is 1 barrel/well/day. This steadily decreases to 13 years at a rate of 15 barrels per day. Even if the produced water is only one barrel/day, the life cycle events caused by water management issues still occur.

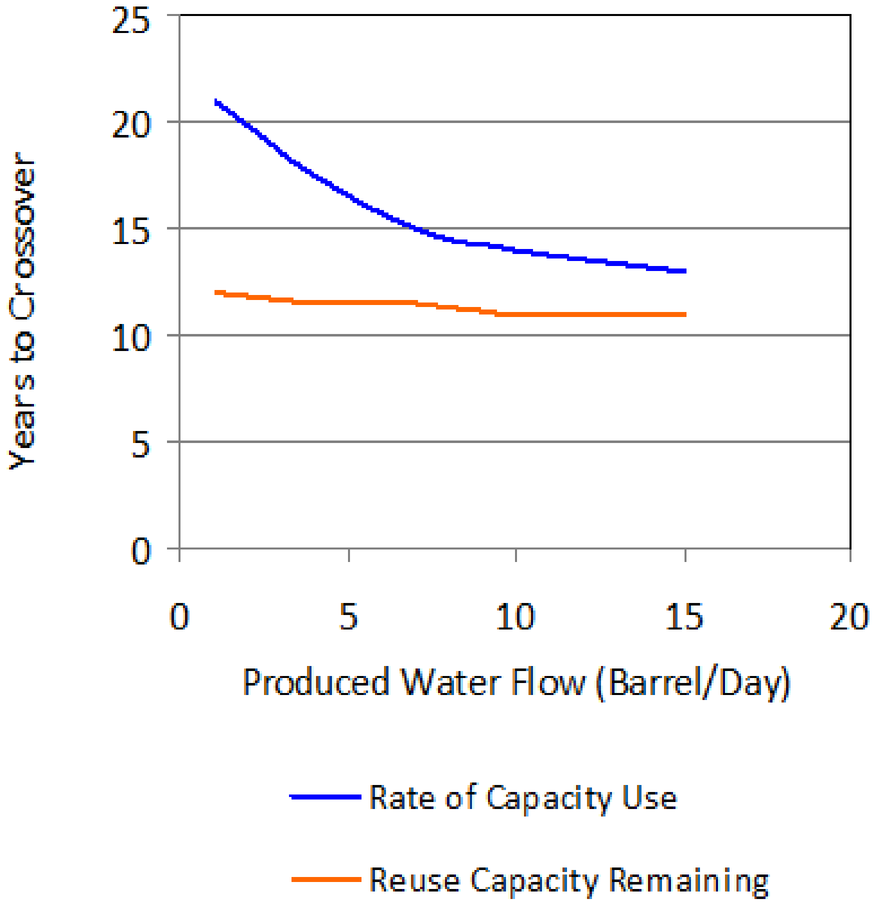


Figure 11-8: Sensitivity Analysis, Definition of the Cross-Over Years in Total Reuse Capacity and Rate of Capacity Use vs Produced Water Flow per Well

Sensitivity: Scheduled Refracture*:* Water management in the Marcellus has the potential to dictate the rate of refracture if an effective strategy that allows for contingencies is not in place. Assuming 4800 wells with three refractures per well, and 7 barrel per day per well of produced water after the flowback event, the grace years until the first cross-over (booked capacity) and critical years (rate of water recovery versus rate of capacity generation) are also a function of the scheduled period between refractures. Figure 11-9 is a sensitivity analysis of the years to cross-over versus the number of days a well operates between refracture events. Based on this plot, there is an optimum rate of refracture that occurs at around 2125 days between refractures at a given well. The driver creating this optimum is the delicate balance between the initiation of refracture and the completion of the last well.

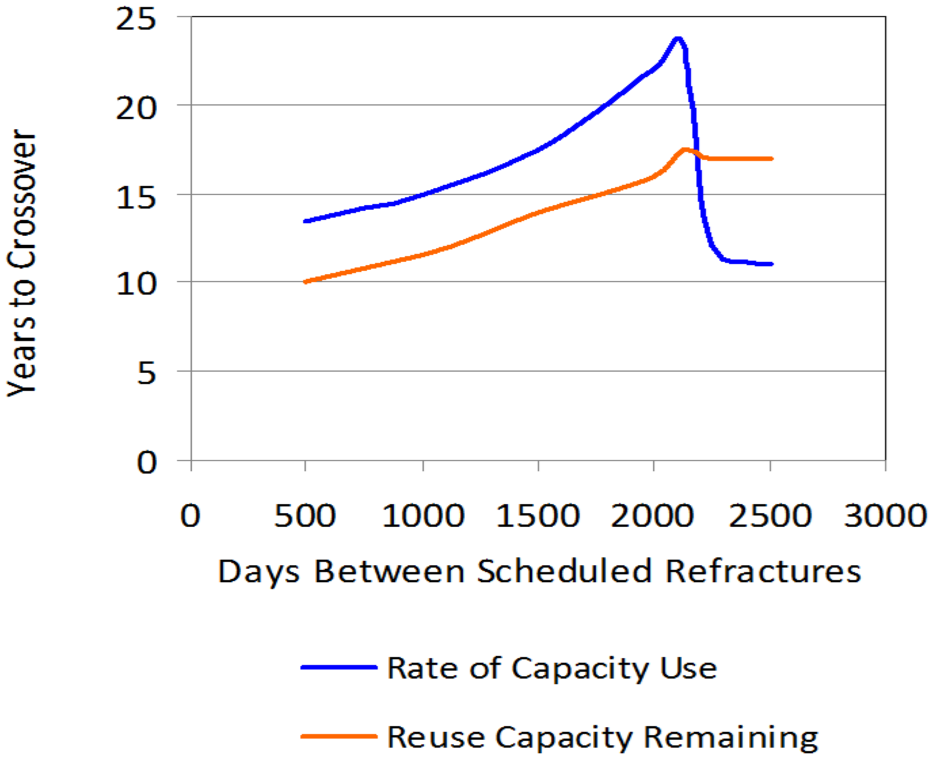


Figure 11-9: Sensitivity Analysis, Effect of Refracture Schedule on Utilization of Reuse Capacity

Year-by-Year Indirect Cost Estimates for the Base Case: The Life Cycle model can be modified to track indirect costs on a year-by-year basis. Hayes and Smith (2011) prepared indirect the cost estimates for carbon footprint, and fuel costs for several management options in the Marcellus. A single case, that in which all non-reuse water is trucked to a deep well requiring a 160 mile round trip is reproduced in Table 11-3. Figure 11-10 shows that the play will generate up to 350,000 truck trips per year with costs up to $31 million in indirect costs (Figure 11-11), and with road repair costs highly dependent on the number of refractures planned (Figure 11-12). These costs grow and then decline along with field activity. In the case of road maintenance, these costs may add 6-7% to the annual hauling costs during peak activity.

*Table 11-3: Estimated Carbon Costs per Truck Mile by Flow Scheme (Marcellus Shale)**

Miles Traveled per Trip	160
Diesel Used (gal)	21.6
CO_2 Emissions (lb)	480
CO_2 Emissions (ton)	0.240
Carbon Cost per Trip	$6.24
Carbon Cost per Barrel	$0.0524
Carbon Cost per Truck Mile	$0.0390
Carbon Cost per Ton CO_2 Emitted	$26

*Hayes and Smith (2011)

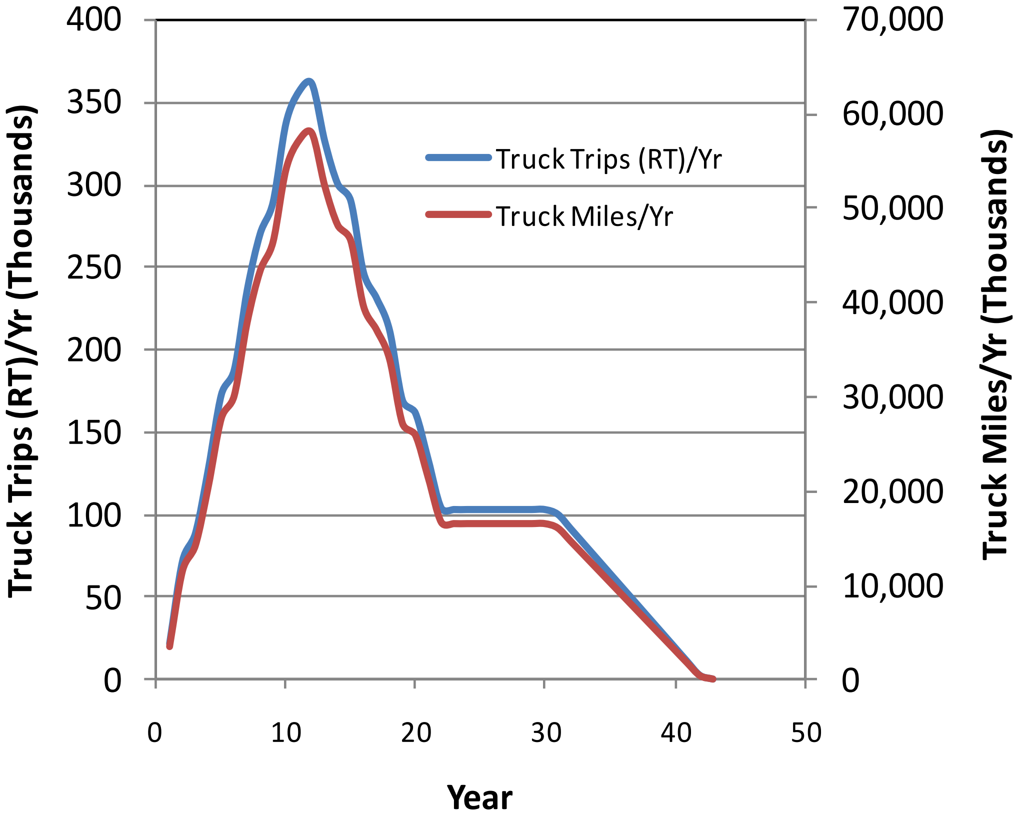


Figure 11-10: Truck Utilization with Deep Well Injection Off-site

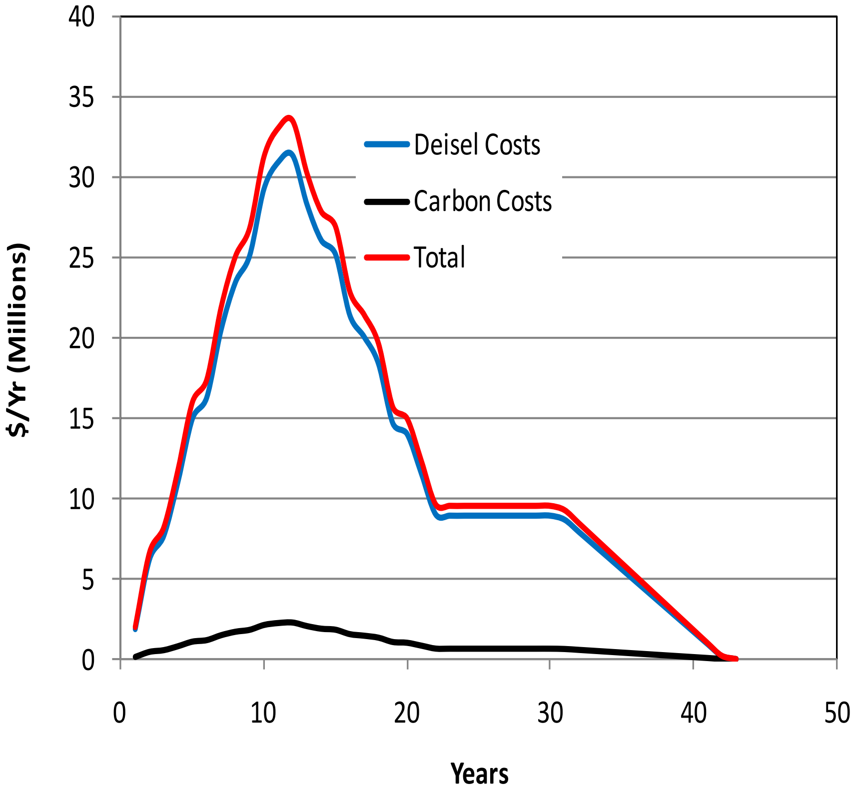


Figure 11-11: Indirect Costs: Carbon Relative to Diesel

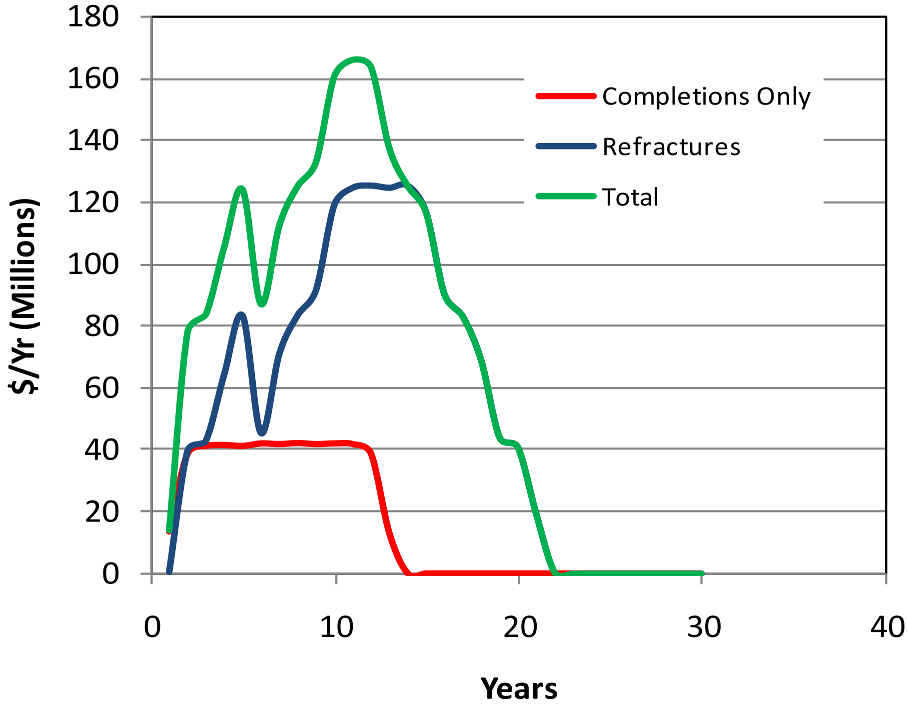


Figure 11-12: Cost of Road Repairs

Deliverables

<u>Topical Report:</u> Hayes, T.D., and Severin, B.F., Preliminary Engineering Systems Analysis of Shale Gas Water Management. RPSEA Report No. 08122-05.10. February 2012.

<u>Completed Manuscripts to be Submitted to SPE in 2012</u>

Severin B.F., Galusky, L.P and Hayes, T.D., Empirical Interpretation of Barnett and Marcellus Flowback Events: Part I, Hydraulic Considerations

Severin B.F., Galusky, L.P and Hayes, T.D., Empirical Interpretation of Barnett and Marcellus Flowback Events: Part II, Brine Profiles

Severin B.F., and Hayes, T.D., Empirical Interpretation of Barnett and Marcellus Flowback Events: Part III, Projection of Wellhead Profiles

Hayes, T.D., and Severin, B.F., Empirical Interpretation of Barnett and Marcellus Flowback Events: Part IV, Life Cycle Projection of a Marcellus Play

Impact to Producers

The overarching goal of this project is to provide the producers with information that helps to 1) minimize fresh water utilization, 2) maximize water reuse, 3) minimize disposal costs, and 4) reduce truck traffic (carbon footprint) throughout a gas play. This task (Task 11 Systems and Life Cycle Analysis) takes a first look at the broad water management issues in the development of a hypothetical play during its development over a 45 year period. The major implication of this development effort is the realization that the water management issues differ throughout the life of the play as the play goes from its youth, to middle-age, to old-age.

In the early development years, water management can be as simple as pre-treatment and reuse in subsequent fractures, as reuse capacity is generated by the fracture of the next well. At some point (***first cross-over year***), the planned recovery of water exceeds the planned generation; and the play passes into middle-age. The recovered water is, on average, more salty. It would be beneficial to implement more aggressive water treatment methods to minimize disposal costs and better match reuse capacity to planned fractures. At another point, not too distant in the future (***second cross-over year***), comes the realization that the rate of water recovery (mostly produced water) exceeds the rate of generation of reuse capacity. The play is in its old age with respect to water management. It is now critical that treatment alternatives are in-place.

Conclusions and Recommendations

Implications: Life cycle analysis of water management issues in shale gas plays is in its infancy. Simplistic projections show that there is a real possibility that water management issues will dictate most of the important decisions in a life of a play. Water management has the potential to dictate how many wells are drilled, the number of refractures planned, the periodicity of the refractures, the need and desirability to reuse recovered water, and ultimately the close-in date of individual wells. This infers that management, economic, and engineering decisions concerning the play should be considered before the first well is drilled.

Outlook: The life cycle and the major events in each play will be unique. It is seen in this simple analysis that the water management concerns in the Marcellus lead to one set of projections. These will be different than in the Barnett, where fresh water is limited; while deep-well injection potential is plentiful. These life cycle implications will also differ for the Eagleford where the baseline groundwater salt concentration appears to be much less than in either the Marcellus or the Barnett. The life-cycle model can be applied to these broad regions, or to specific well fields, based on the availability of the hydraulic and salt databases. These operational profiles may be taken into account in the fine tuning of a life cycle analysis and will yield different projections.

Value: The value of this development effort was to open a new dialogue concerning the long term water management issues facing the development of shale gas plays. New terminology was established to define the progression of the play from its youth to middle age to old age, with definable cross-over years. These clearly defined management periods also connect the water engineering needs to the projected events in the field. These events can be forecast in economic terms, allowing for more rational and informed business decisions. Since water management can amount to tens of millions of dollars per year for a single county-sized development area, it is well advised that companies use water management forecasting as one additional tool in their sustainability planning and in accounting pro-forma analyses in the financial management of shale gas business operations and future investment decisions.

Future Considerations: The life cycle model is amenable to inclusion of new data bases. The model may be modified, as needed, for other regions of the world. Fore-knowledge of expected water conditions will allow for better engineering and implementation of water treatment technologies.

12 Technology Transfer

In parallel with the performance of the tasks of this project, GTI and its team have pursued opportunities for technology transfer through presentations at workshops and technical meetings, generation of topical reports to be disseminated by RPSEA and through the creation of publications in journals.

During the project, presentations were made at 12 technology transfer events as listed in Table 12-1. These forums included five workshops. The workshops accomplished timely transfer of information of the RPSEA project to the state regulators attending the Groundwater Protection Council Water/Energy Events in 2010 and 2011, to the water management utility stakeholders attending the American Water Works Research Foundation in 2011, and the Federal regulators attending the USEPA Workshop on Shale Gas Water Management in 2011 at which GTI served as facilitator of the water treatment session of the 4th Workshop. Copies of all of the presentations of Table 12-1 have been uploaded to the RPSEA Website. Presentations were also given at three workshop forums that were sponsored by RPSEA.

Table 12-1: List of Presentations (Technology Transfer)

Title of Presentation	Forum	Date
1. Produced Water Challenges and Opportunities	Houston Gas Processors Association Meeting	January 20, 2010
2. Produced Water Research Projects	RPSEA Unconventional Gas Conference 2010, Golden CO	April 7, 2010
3. Development of Technologies for the Reuse of Flowback and Produced Waters Associated with Shale Gas Production	International Coalbed & Shale Symposium, Tuscaloosa, Alabama	May 20, 2010
4. Panel and Discussion - Shale Gas and Water: Myth Versus Reality	GTI Global Unconventional Gas Symposium, Amsterdam	June 17, 2010
5. Shale Gas Water Management Consortiums: Marcellus and Barnett	Groundwater Protection Council (GWPC) Water/Energy Workshop, Pittsburgh	September 27, 2010
6. Workshop on Natural Gas Development Issues for Drinking Water Utilities	American Water Works Association Research Foundation (AwwaRF), Baltimore, MD	October 18, 2010
7. Shale Gas Water Management Consortiums: Marcellus and Barnett Regions	Groundwater Protection Council (GWPC) UIC Workshop, Austin, TX	January 24, 2011
8. Characterization of Marcellus and Barnett Shale Flowback Waters and Technology Development for Water Reuse	USEPA Workshop on Shale Gas Water Management, Arlington, VA	March 30, 2011
9. Techno-Economic Assessment of Water	Shale Gas Water	April 13, 2011

Title of Presentation	Forum	Date
Management Solutions	Management Initiative, Canonsburg, PA	
10. Overview of RPSEA Water Management Programs	WSCOGA Environmental Summit, Grand Junction, CO	October 27, 2011
11. Issues and Challenges Associated with the Management of Flowback Water Associated with Shale Gas Development	18th Annual International Petroleum & Biofuels Environmental Conference, Houston, TX	November 8, 2011
12. Key Note Presentation on Shale Gas Water Management	DUG East Technical Workshop: Water Management and Environmental Procedures, Pittsburgh, PA	November 15, 2011

The GTI project has also made all of its topical reports, monthlies and the Final Report available in electronic format to facilitate distribution; reports have been designed to not exceed 8 megs in size to allow easy downloading and transfer via email to promote ease of technology transfer. A complete list of deliverables from Contract 08122-05 is presented in Table 12-2. All of these products have been uploaded to the RPSEA SharePoint Site for eventual distribution through the RPSEA Website. Further, the project has supported the improvement of the website of the Barnett Shale Water Conservation and Management Committee (BSWCMC) to promote communication of best practices to the industry and to stakeholders and to serve as an industry portal through which the most relevant topical reports from the GTI project can be distributed. Reports have been transferred to the BSWCMC for informal industry review; upon approval from RPSEA, the reports will be made available for distribution from the BSWCMC website (www.barnettshalewater.org) .

Table 12-2: Complete List of Deliverables from Contract 08122-05

Order	Description / Title	Task	Authors
A	Project Management Plan	1	Thomas Hayes
B	Technology Status Assessment	2	Thomas Hayes
C	Water Characterization Information Base in Excel Spreadsheet.	4	Thomas Hayes
1	Development of Electrodialysis for Shale Gas Water Reuse. RPSEA Report No. 08122-05.01. November 2010.	8	Blaine Severin Thomas Hayes
2	Membrane Fouling Reduction Test Plan – Processing Shale Gas Flowback and Produced Water. RPSEA Report No. 08122-05.02. December 2010.	10	Steve Shiner Robert Hayes Dileep Agnihotri Richard Li Xiaofei Huang Peach Sirirat

Order	Description / Title	Task	Authors
			Albert Li
3	Innovative UF / NF / RO Membrane Performance Through the Use of Innovative Coatings: Selection of Membrane Supports and Coatings for Barnett Well Flowback Water Separations. RPSEA Report No. 08122-05.03. November 2010.	9	Albert Li Sirirat Kasemset Daniel J. Miller Benny D. Freeman Mukul M. Sharma
4	Feasibility of Using Alternative Water Sources for Shale Gas Well Completions – A Preliminary Guidance Document on the Current Practices in the Barnett. RPSEA Report No. 08122-05.04. February 2011.	6	Jean-Philippe Nicot
5	Field Assessment and Anti-Fouling Polymeric Membrane Coatings for Treatment of Barnett Shale Flowback Produced Water. RPSEA Report No. 08122-05.05. March 2011.	10	Xiaofei Huang Dileep Agnihotri Benny D. Freeman Robert Hayes Sirirat Kasemset Albert Lee Hua Li Mukul Sharma Steve Shiner
6	Feasibility and Design Approach for Automatic Classification and Segregation of Early Flowback Water for Reuse in Shale Gas Hydraulic Fracturing. RPSEA Report No. 08122-05.06. July 2011.	5	L. Peter Galusky
7	Feasibility Assessment of Early Flowback Water Recovery for Reuse in Subsequent Well Completions. RPSEA Report No. 08122-05.07. October 2011.	5	L. Peter Galusky
8	Feasibility of Using Alternative Water Sources for Shale Gas Well Completions. RPSEA Report No. 08122-05.08. January 2012.	6	Jean-Philippe Nicot
9	Characterization of Flowback Waters from the Marcellus and the Barnett Shale Regions. RPSEA Report No. 08122-05.09. February 2012.	4	Thomas D. Hayes Blaine F. Severin
10	Preliminary Engineering Systems Analysis of Shale Gas Water Management. RPSEA Report No. 08122-05.10. February 2012.	11	Thomas D. Hayes Blaine F. Severin
11	Engineering Decision Tool for the Evaluation of Mechanical Vapor Recompression for the	7	Thomas D. Hayes Blaine F. Severin

Order	Description / Title	Task	Authors
	Treatment of Shale Gas Flowback Water. RPSEA Report No. 08122-05.11. February 2012.		
12	Evaluation of Electrodialysis in the Demineralization of Shale Gas Flowback Waters. RPSEA Report No. 08122-05.12. February 2012.	8	Blaine F. Severin Thomas D. Hayes
13	Novel Fouling-Resistant Membranes for Barnett Shale Water Management and Reuse. RPSEA Report No. 08122-05.13. February 2012.	9	Albert Lee Sirirat Kasemset Daniel J. Miller Benny D. Freeman Mukul M. Sharma
14	Final Report: Barnett and Appalachian Shale Water Management and Reuse Technologies. RPSEA Report No. 08122-05.14. February 2012	13	Thomas D. Hayes Blaine F. Severin

Lastly, the results of the RPSEA-NETL supported work has led to the preparation of 14 publications that will be submitted to the scientific journals in 2012. These publications are listed in Table 12-3; all but two of the manuscripts have been prepared. These manuscripts will be submitted for RPSEA review in first half of 2012.

Table 12-3: 14 Publications Arising from the Project

Team Organizations	Description of Publication	Project Task	Status
GTI and Range Resources	Characteristics of Shale Gas Flowback Water in the Marcellus Play	4	Completed Draft Under Review by Marcellus Industry
GTI and EPD	Five Publications on ED Research Findings	8	Completed
GTI and EPD	Four Publications on Water Based Life Cycle Modeling	11	Completed
GTI, EPD, and Industry Cooperators	Field Evaluation of Mechanical Vapor Recompression in the Treatment of Flowback Water	7	Completed and Under Review.
UT, Advanced Hydro	Innovative Coatings for Ultrafiltration and Reverse Osmosis Treatment of Shale Gas Waters	9	Pending

Team Organizations	Description of Publication	Project Task	Status
UT, GeoPure, Advanced Hydro, GTI	Field Evaluation of Coated Membranes in the Treatment of Flowback Water	10	Completed
BEG, GTI	Development of Alternate Water Sources for Sustainable Shale Gas Development in the Barnett	6	Pending

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GeoPure Hydro Technologies, Fort Worth, TX
Stat Analytical, Chicago
Test America, Pittsburgh, PA
Texerra, Monument, CO
Xenco, Ft Worth, TX

In-kind cost share was provided by Devon Energy. Mechanical vapor recompression (MVR) equipment evaluated in the field was manufactured by AquaPure and operated by Fountain Quail. Commercial partner of the University of Texas is Advanced Hydro for the commercial introduction of coated membranes based on UT's IP. GeoPure is a skid equipment testing company that is continuing to use the coated membrane products in their shale gas water treatment operations.