Oil & Natural Gas Technology

DOE Award No.: DE-FE0001466

Quarterly Report 3 (3/1/10 – 6/30/10)

Zero Discharge Water Management for Horizontal Shale Gas Well Development

Submitted by:

West Virginia Water Research Institute
West Virginia University
PO Box 6064
Morgantown, WV 26506

Authors:

Jennifer Fulton
Paul Ziemkiewicz, PhD
Doug Patchen, PhD
David Locke
Harry Johnson
Ray Lovett, PhD

Prepared for:

United States Department of Energy National Energy Technology Laboratory

Acknowledgment:

"This material is based upon work supported by the Department of Energy under Award Number DE-FE0001466."

Disclaimer:

Executive Summary:

Major effort this quarter was devoted to testing technologies needed to produce a water quality suitable for the next fracture treatment. Particulates greater than approximately 3 microns were completely removed from one Marcellus raw water sample by the FilterSure PDU now installed at the WVU high bay area. A second Marcellus sample was shipped to a provider of Electrical Coagulation (EC) technology for testing. The EC treated water was returned to WVU and, after filtering, produced a visually clear liquid. Chemistry results show that EC followed by filtration will adequately condition the water for recycle. Funds originally scheduled to complete the Phase I work beginning October 1 have been reprogrammed. All of the Phase I work will now be completed by September 30, including

a continuous process demonstration at the University that links the EC and the FilterSure technologies to verify performance and to establish process economics.

Progress Report– Phase I

This progress report covers the progress of the Phase effort from **3/1/10 to 6/30/10**. The report is organized by task as listed in the Statement of Project Objectives.

PHASE I /Budget Period 1

Task 1.0 – Project Management and Planning

Work planned in the prior quarter was initiated. A chemical hygiene plan was developed for both the PDU filtration and the bench-scale work. Both have been approved by the NRCCE Facilities Manager, the NRCCE Chemical Hygiene Officer, and WVU Environmental Health and Safety. A Technology Status Report was compiled and submitted.

In lieu of an Industry Contact Group meeting, we developed and sent a detailed questionnaire to the members of our Industry Contact Group in order to gain more information in a shorter period of time. We have received responses from four producers, and anticipate receiving more. This has provided extremely useful information regarding water volumes and parameters necessary for recycling of frac water. In addition, we met with representatives from a company in our Industry Contact Group to show the PDU, and discuss plans for obtaining data and water samples from wells around the region, as well as possibilities for deployment of the Mobile Treatment Unit in Phase II of the project.

The 2-GPM FilterSure Process Development Unit (PDU) was prepared for shipment from its New Jersey location to WVU. The 1,600-pound PDU was delivered in February and testing was initiated. Test results were reviewed at a March project planning meeting held at the University. These results were sufficiently encouraging (discussed in Task 2.4) to warrant testing Electro Coagulation (EC) as a second component of a commercial process train. Members of the project team toured a Marcellus Shale gas well site, and obtained a large volume (130 gallon) frac water sample from a member of our Industry Contact Group. This sample was treated by an EC vendor and returned to the University for filtration. A high TDS sample (185,000 mg/L) was also obtained from an industry partner. This sample will be used in the continuous process demonstration now scheduled for early August.

Task 2.1 Develop Conceptual Process Train

A conceptual process train is being developed around the FilterSure technology and equipment needed to support this technology. With the currently available data (summarized in Tasks 2.2 and 2.4) the EC followed by the filter will produce water with virtually no solids. The need for subsequent processing to reduce Total Dissolved Solids (TDS) does not appear to be necessary. Acceptable recycle water quality has been identified in industry responses to the questionnaire provided by our Industry Contact Group. Information provided by Group members contains water chemistry requirements for recycling flow back water. Members of the Industry Contact Group also supplied frac return-water samples from shale wells in the region, and more water samples have been promised. We are continuing to process these samples to obtain water chemistry and suspended solids characteristics.

Collecting a representative frac water sample proved to be a key issue and was subject to some debate. Did we need samples of frac flow-back at different times (e.g., early, middle, *and* end of the flow-back)? Should samples be obtained directly from the flow-line or at some other point? After discussing this issue with industry personnel, we concluded that evaluating flow-back samples over time was impractical and unnecessary. The most practical approach is to sample only the water that would likely be treated; i.e., water from the frac return-water storage tanks or pits.

Recycle water quality criteria have been established and will continue to be vetted with our Industry Contact Group. Solids removal efficiency has been established by laboratory testing of the Marcellus samples we have received. This information quantifies the volume of solid materials that will need to be managed during commercial operations, a critical variable in developing a conceptual process train.

Task 2.2 Develop Process Flow Model:

Initial results show that EC followed by filtration will adequately condition the water for recycle from a solids loading perspective. The ability to remove heavy metals and other targeted materials is presented in Tables 1, 2, and 3. These results show that the EC followed by filtration will remove 28% of the dissolved solids and 27% of the total solids. Based on these results, additional downstream treatment will not be needed. Accordingly, our preliminary process flow includes only EC followed by filtration.

Table 1 Total Dissolved Solids Results, Sample 3EC

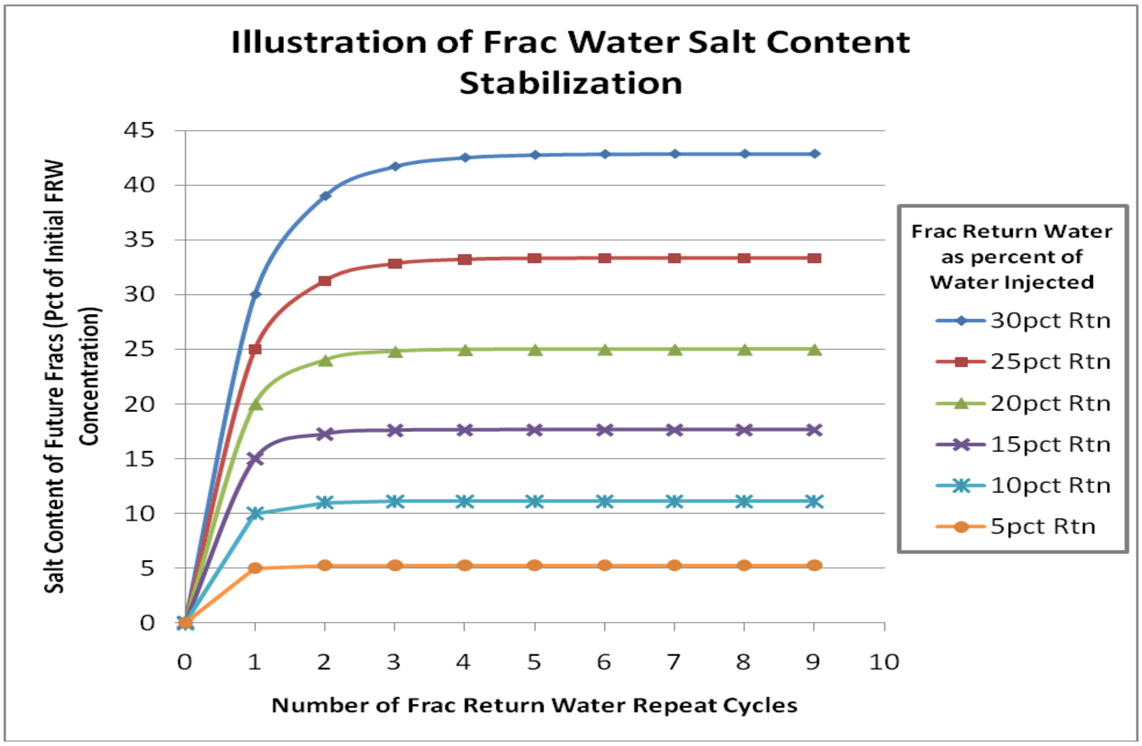
Table 2 Total Solids Results, Sample 3EC

Table 3 Other Results, Sample 3EC

Task 2.3 Identify Recycling Operational Requirements

The recycled water can be reused indefinitely. The water doesn't wear out and the process of combining mostly fresh water with a lesser amount of salty water will result in a relatively constant mix after a few re-uses – i.e., recycling frac water does not increase its saltiness forever. For a given development region, the maximum saltiness of water mixtures used for any subsequent frac treatment should quickly max-out as a function of average frac water return. This stabilization (maximum salt concentration) occurs by the 3rd repeat cycle as shown by the following figure. The salt concentration would be the same for the 4th frac cycle and remain constant for all subsequent frac jobs.

For example, if the typical frac water return is 15%, and initial frac return water salt content is 60,000 mg/l, then the stabilized salt concentration (TDS) is 10,600 mg/l. If the initial TDS is 100,000 mg/l, the stabilized frac fluid would be 17,600 mg/l.



Task 2.4 Develop and Test Treatment Methods

Cost of Water Treatment

A program that calculates the unit costs of various treatment methods is being updated by the addition of some new methods (such as the FilterSure system and EC) and current prices. Table 1 shows costs per 1000 gallons for a number of treatments, including EC. The EC method appears to be competitively priced among the various options.

Figures 1 – 3 detail some initial investigations comparing nanofiltration, which preferentially separates divalent ions, and reverse osmosis. These are two proposed technologies for TDS removal. The graphs compare cost versus process efficiency, cost versus flow, and cost versus electricity cost. In all instances nanofiltration is cheaper because of its lower pressure requirements. The rise in cost at low efficiency for the first plot is due to increasing reject disposal costs. Low flow also increases the cost due to the fixed costs associated with the system. The increase in cost due to electricity rates is almost linear. Improved data are being added to the database.

Table 1. Costs of various treatment methods

Treatment Method	$/1000 gallons
Surface disposal	$0.07
Deep injection well - existing	$0.66
Evap/infil pond w/ spray	$0.99
Spray Irrigation	$1.08
Microfiltration	$1.36
Evaporative pond - Lined-Spray	$1.97
Electrocoagulation	$2.00
Shallow injection/aquifer renewal	$2.85
Evaporative pond/infiltration	$2.98
Water hauling	$4.82
Deep injection well - new	$5.64
Nanofiltration	$6.15
Reverse Osmosis	$6.94
Evaporative pond - Lined	$27.56

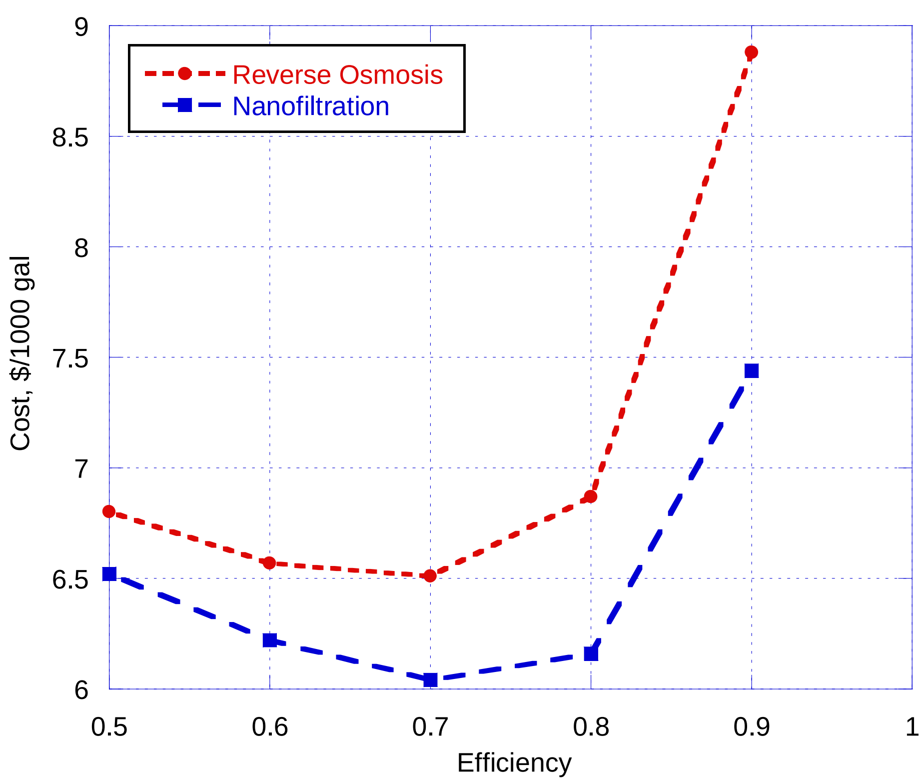


Figure 1. Comparison of cost and efficiency between nanofiltration and reverse osmosis

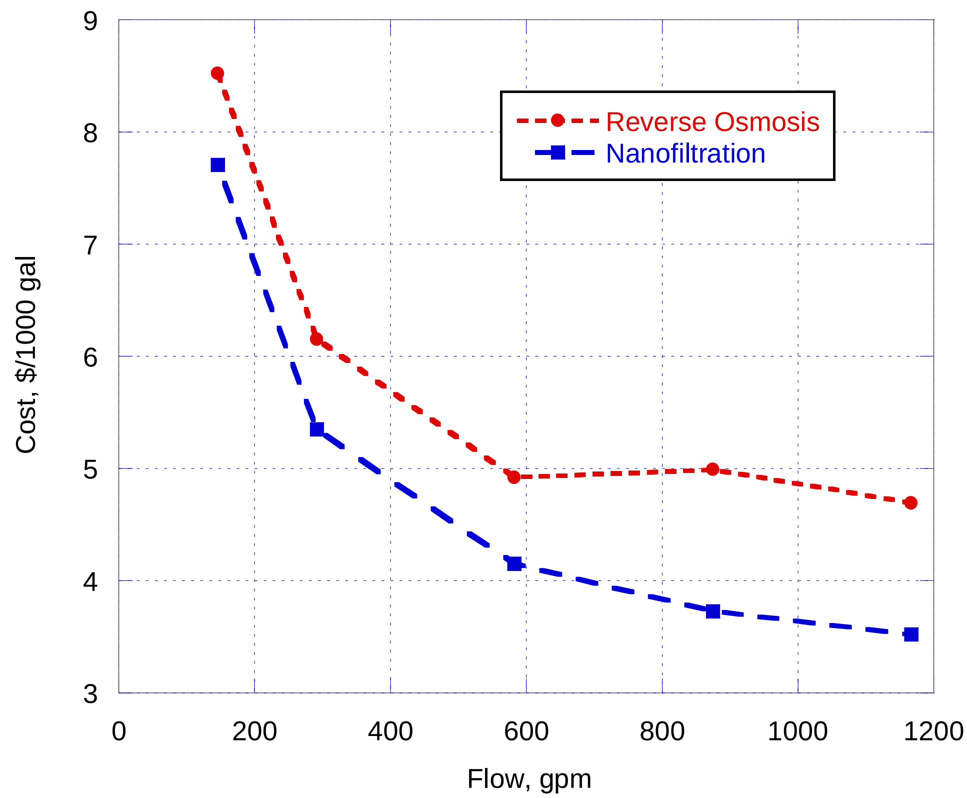


Figure 2. Comparison of cost and flow between nanofiltration and reverse osmosis

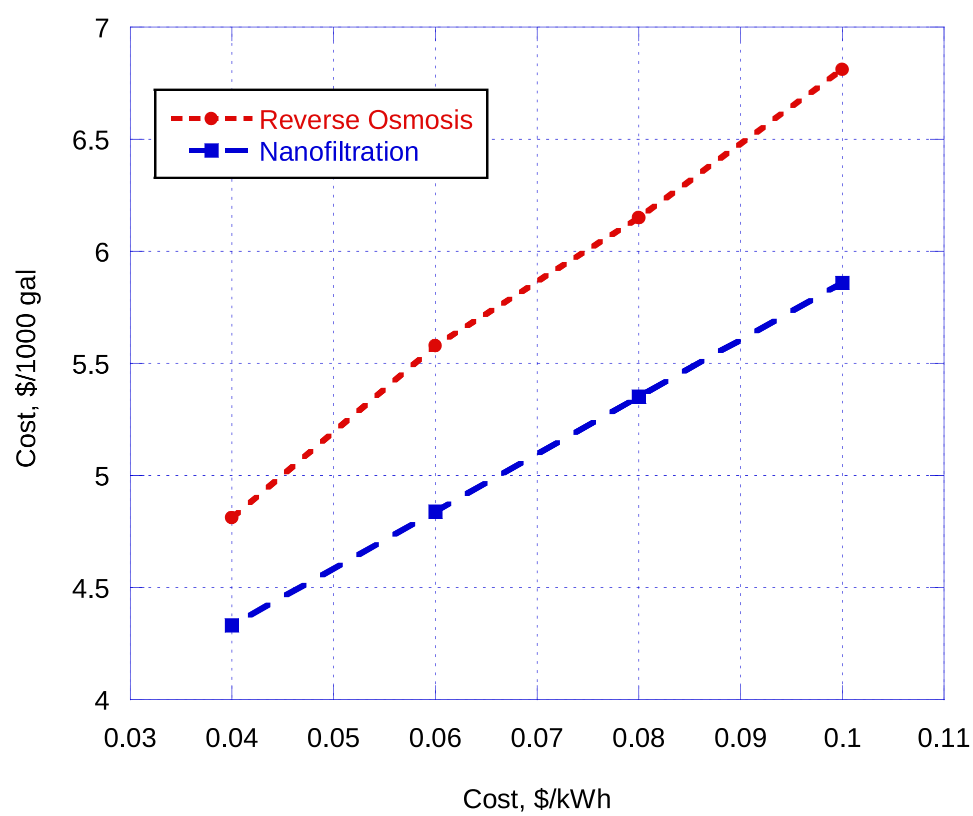


Figure 3. Comparison of cost and electricity cost between nanofiltration and reverse osmosis

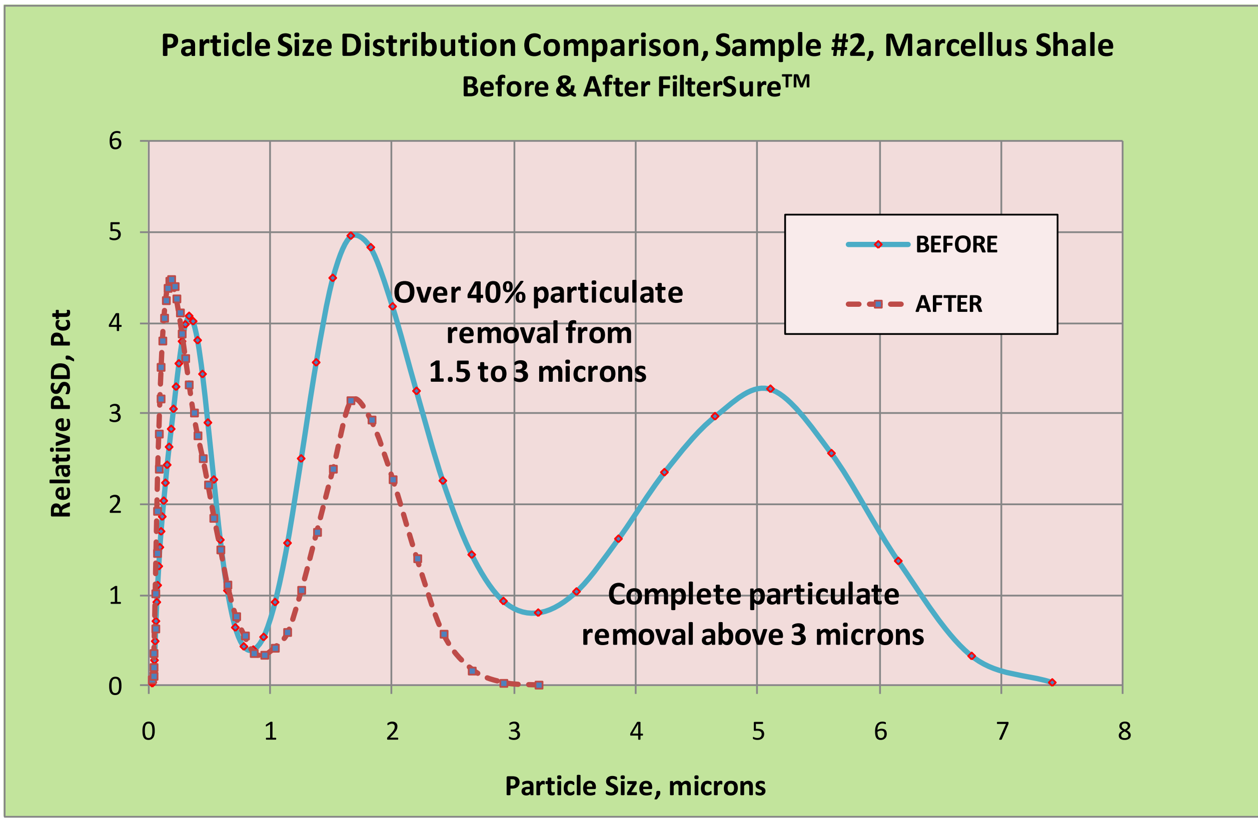


Figure 4. Particle size distribution following FilterSure™ PDU test on Marcellus water

Upstream Technologies

Major effort this quarter was devoted to testing both the FilterSure and the EC technology as key upstream process technologies. Raw water from one Marcellus sample was filtered by the FilterSure 2-GPM PDU. Figure 4 plots the Particle Size Distribution (PSD) as a percent of the total particles vs. the particle size in microns. Results show that particles greater than approximately 3 microns were completely removed from the water sample by the FilterSure technology. Additionally, particles larger than about 1 micron were reduced by an estimated 40%.

A second Marcellus sample provided by an industry partner was shipped to a provider of Electrical Coagulation (EC) technology for testing as a potential pre-treatment option. The EC treated water was returned to WVU for evaluation. The results (presented in Figure 5) show that the EC technology had a major impact on the distribution of the solids.

Specifically, the EC technology caused the solids to shift from a few microns in size to larger solids having a normal bell shaped distribution. Heavy metals and/or radioactive compounds are expected to be contained in the EC mobilized solids that will be removed by filtration and managed as a part of a commercial process.

Using the particle size distribution results, FilterSure selected filter media needed to remove the larger EC produced solids. The EC treated water was processed through the FilterSure PDU with the tests witnessed by DOE and other representatives. Effluent from the PDU was visually clear without particulates. Water chemistry of the effluent, reported in Tables 1, 2, and 3 in Task 2.2 above, show the water chemistry to be acceptable for recycling.

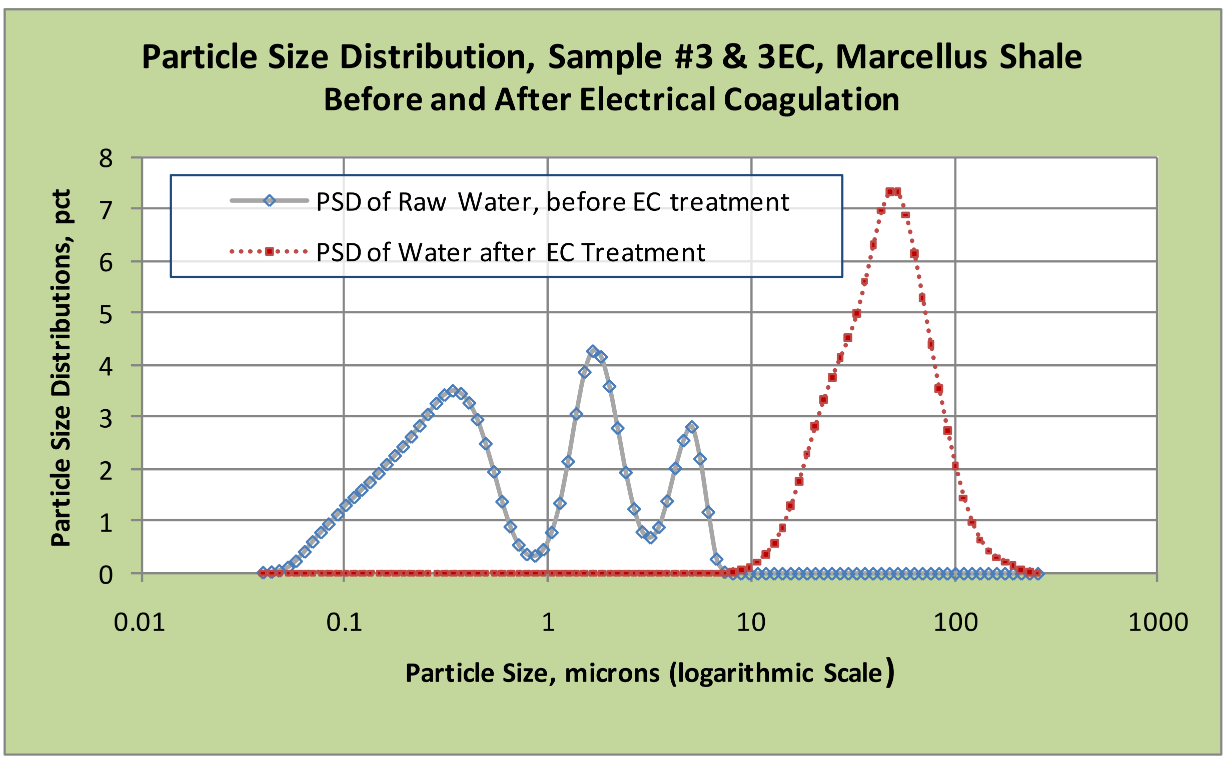


Figure 5. Particle size in raw and EC treated Marcellus water

Removal of Salt Using Solvents

Methods for measuring the effect are being developed. The solubility determined for KCl (mean of 3 trials) was 34.5g/100g water.

Investigations of mixed solvents began using 2-propanol. Solubilities and conductivities were evaluated. The solubility of KCl in 2-propanol/ water mixtures [Figure 1], for example, shows that the initial 26% KCl by weight drops to nearly 1% when the solvent is 80% 2-propanol by weight. The concentration when referenced to the original water decreased from $3.45x10^5$ mg KCl/kg water (roughly 345,000 mg/L) to $4x10^4$ mg KCl/kg water (~40,000 mg/L). Removal of the precipitated salt, then removal of the 2-propanol would result in an 88% reduction of salt. This removal can be seen more clearly in Figure 2, where KCl removal is plotted versus the mass of 2-propanol added.

Evaluation of salt removal by the addition of solvents is best monitored using the conductivity of the system. Initial investigation of the relationship indicates that a solvent based derivable relationship exists, as demonstrated by Figure 3.

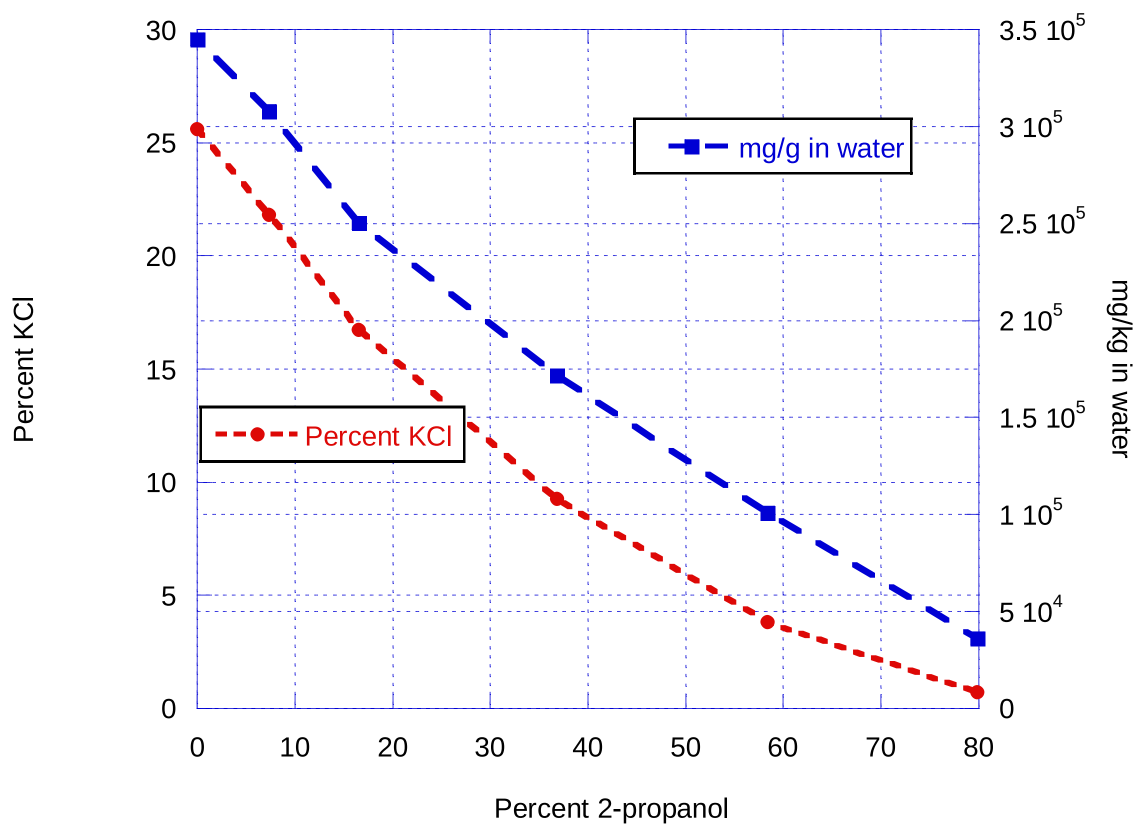


Figure 6. Removal of KCl from a saturated solution by the addition of 2-propanol.

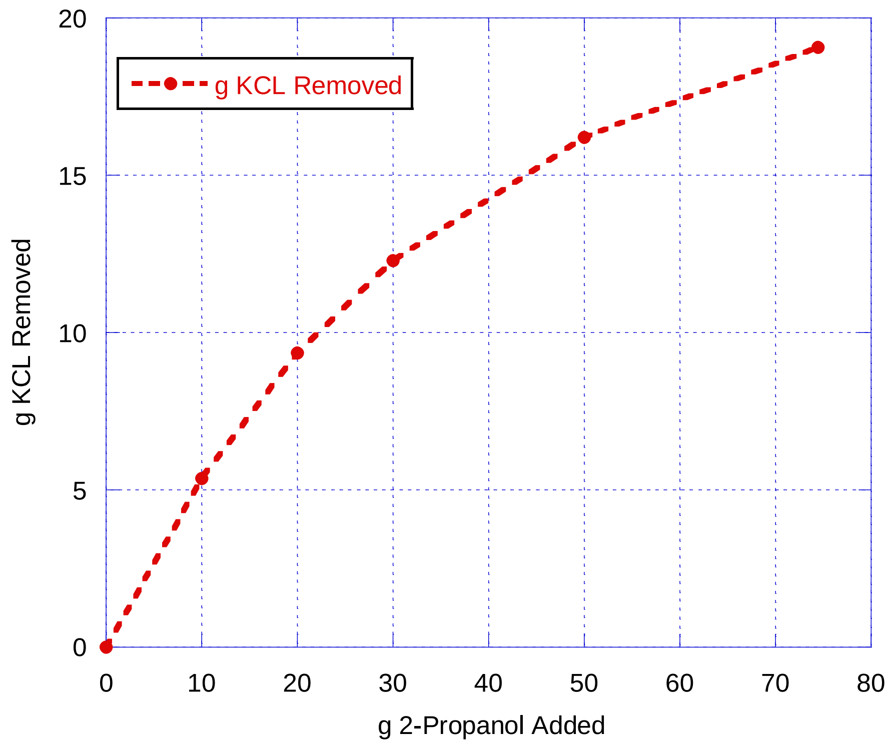


Figure 7. Grams of KCl removed by adding 2-propanol to an aqueous solution originally containing 25.6g KCl

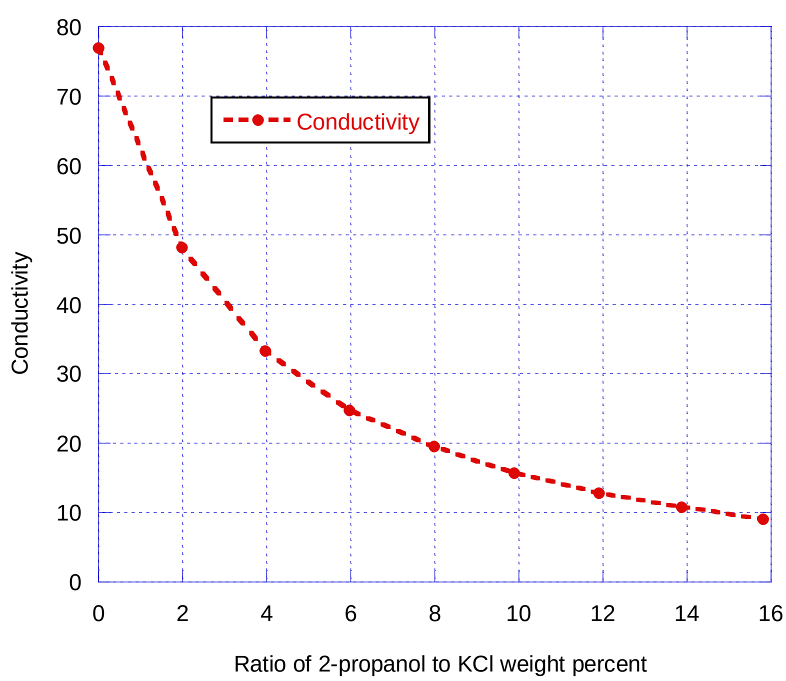


Figure 8. Conductivity vs. ratio of 2-propanol to KCL

Issues & Challenges:

The excellent cooperation of our Industry Contact Group in providing frac water samples has resulted in a high burn rate on year-one funding for FilterSure. As a result, the funds originally planned to complete Phase I have been reprogrammed to this Fiscal Year. All of the Phase I work will therefore be completed by September 31, 2010.

Milestone Report:

Milestones in tasks 2.1, 2.2, and 2.3 were completed. We expect to be able to accomplish all milestones on schedule.

Cost Status Report:

Overall project costs are detailed in Appendix A. A new fiscal task was created in order to pay a graduate research assistant within the WVU Department of Civil and Environmental Engineering to complete the particle size distribution analysis and provide experimental support for the removal of salts using solvents.

FilterSure installed its 1,600 pound PDU in the WVU high bay research area. Setup costs and the costs of two complete filtration tests have largely exhausted FilterSure subcontract funds planned for year 1. During this quarter, the remaining Phase I funds were made available and FilterSure is completing the remaining scheduled experimental work. For this effort, we have secured a high (185,000 mg/L) water sample. A EC unit was rented from a vendor and moved to the WVU laboratory. A continuous process demonstration that links the EC and the FilterSure technology is scheduled for early August and this test will help to establish process economic feasibility.

Summary of Accomplishments:

The project is currently ahead of schedule, but with corresponding costs higher than originally scheduled. Significant accomplishments this quarter are listed below:

- An Industry Contact Group was created to gain information on operating parameters and to obtain representative water flowback samples.
- Responses to a questionnaire developed for this project are providing engineering information on volumes of flow back water and water chemistry requirements for recycling of flow back water.
- Industry Contact Group members have provided four flowback frac water samples through the end of this quarter. The WVU Radiation Safety Department tested all samples for radioactivity and found all to be at or below background values. A faculty member and his graduate research assistant in the WVU Department of Civil and Environmental Engineering is determining particle size distribution measurements for each sample received and tested under this program. The WVU analytical la is measuring water chemistry. A commercial lab was engaged to independently check analytical results.
- Tests of one Marcellus water sample show that the FilterSure PDU will remove 100 % of the frac water suspended solids greater than three microns.
- EC shifted the distribution of the suspended particles creating larger size particles as compared with the raw water sample.
- Suspended solids in the EC treated water were easily removed with the FilterSure technology resulting in an effluent that was visually clear without particulates.

Appendix A: Cost Status Report

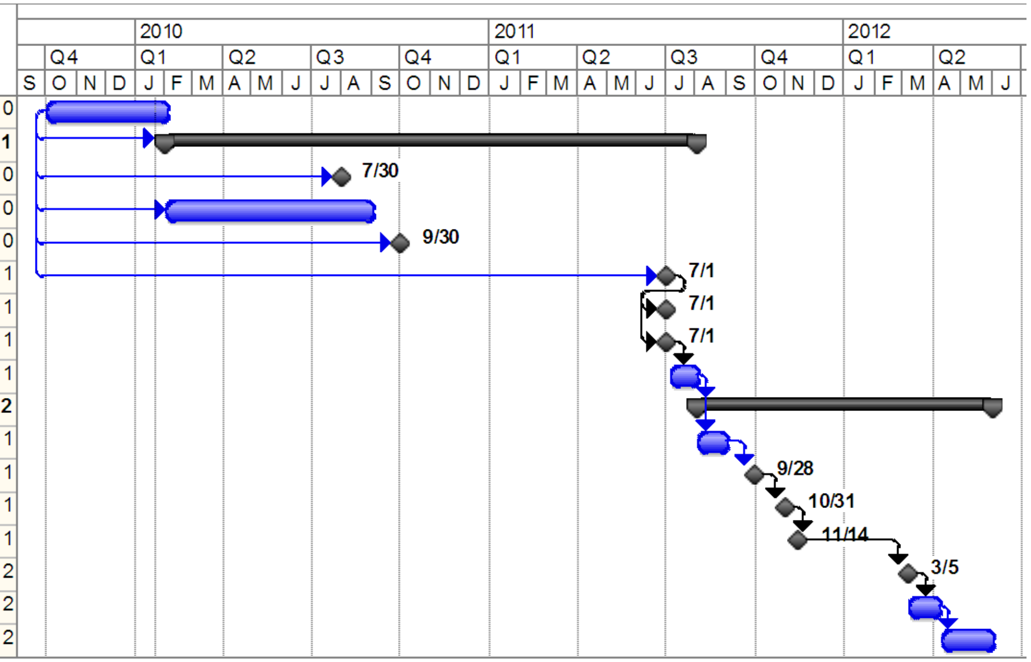
As of Jul 21, 2010	WVWRI	Cost Share WVWRI	NRCCE	Cost Share NRCCE	Graduate Student
Expenditure Category	**Unobligated Balance**	**Unobligated Balance**	**Unobligated Balance**	**Unobligated Balance**	**Unobligated Balance**
	Task 1	Task 2	Task 3	Task 4	Task 5
Salaries Total Unobligated	$2,151.36	($1,815.07)	$2,553.44	$1,000.00	($7.38)
F&A	$30,242.73	0	$1,723.17	0	$0.00
Fringe Benefits	$840.64	($414.93)	$1,151.83	$270.00	($15.80)
General Expenses	$16,274.76				
Subcontractors	$0.00				
Travel	$393.07				
TASK TOTAL	**$49,902.56**	**($2,230.00)**	**$5,428.44**	**$1,270.00**	**($23.18)**
TOTAL WVU					**$54,347.82**

	External Cost Share	
Subcontractor	**Current Budget**	**Unobligated Balance**
FilterSure	$18,000.00	$ 15,789.90
ShipShaper	$11,600.00	$ 1,437.50
TOTAL EXTERN	**$ 29,600.00**	**$ 17,227.40**

Appendix B: Milestone Status Report

Milestones in tasks 2.1, 2.2, and 2.3 were completed. Progress is being made on future milestones, and these will be accomplished on schedule. There is currently no slip in our timeline. Milestones are shown in the Gantt chart below, indicated with diamonds.

Task Name	Start	Finish
Task 1.0 Project Management Plan	10/1/09	2/1/10
Task 2.0 Phase I Process Development	**2/1/10**	**8/1/11**
Subtask 2.1 Develop Conceptual Process Train	2/1/10	7/30/10
Subtask 2.2 Develop Process Flow Model	2/1/10	8/31/10
Subtask 2.3 Identify Recycling Operational Requirements	2/1/10	9/30/10
Subtask 2.4 Develop and Test Treatment Methods	2/1/10	7/1/11
Treatment Method Development Final Recommendations	7/1/11	7/1/11
Subtask 2.5 Preliminary Cost Estimate/Development of Decision Criteria	3/14/11	7/1/11
Subtask 2.6 Decision to Proceed	7/4/11	8/1/11
Task 3.0 Phase II Mobile Unit Design, Test, and Evaluate	**8/2/11**	**5/31/12**
Subtask 3.1 Finalize System Design and Costs	8/2/11	8/31/11
Subtask 3.2 Fabricate Mobile Treatment Unit (MTU)	9/1/11	9/28/11
Subtask 3.3 Install the MTU	9/29/11	10/31/11
Subtask 3.4 MTU Testing and Startup	11/1/11	11/14/11
Subtask 3.5 MTU Operations, Monitoring, and Maintenance	11/15/11	3/5/12
Subtask 3.6 MTU Decommissioning	3/6/12	4/6/12
Subtask 3.7 MTU Demonstration Report	4/9/12	5/31/12



Milestone Log

Task/ Subtask #	Project Milestone Description	Planned Start Date	Planned End Date	Actual Start Date	Actual End Date
2.1/2.2	Complete Conceptual Process Train and Flow Model	2/1/10	5/31/10	2/1/10	projected: 7/31/2010
2.3	Recycling Requirement Identification	2/1/10	4/30/10	2/1/10	4/30/10
2.4	Treatment Method Development Preliminary Findings	2/1/10	7/31/10	2/1/10	
2.4/2.5	Treatment Method Development Final Recommendations including Preliminary Cost Estimate	2/1/10	8/31/10	2/1/10	
2.6	Go/No Go decision to proceed to Phase II	9/1/10	9/30/10		
3.1/3.2	Mobile Treatment Unit (MTU) Design and Fabrication	10/1/10	3/31/11		
3.4	MTU Installation & Startup	4/1/11	4/30/11		
3.5	MTU Field Test	5/1/11	7/31/11		
3.6	MTU Decomissioning	8/1/11	8/31/11		
3.7	MTU Demonstration Report	9/1/11	9/30/11		

National Energy Technology Laboratory

626 Cochrans Mill Road

P.O. Box 10940 Pittsburgh, PA 15236-0940 3610 Collins Ferry Road

P.O. Box 880 Morgantown, WV 26507-0880

One West Third Street, Suite 1400 Tulsa, OK 74103-3519

1450 Queen Avenue SW Albany, OR 97321-2198

2175 University Ave. South Suite 201 Fairbanks, AK 99709

Visit the NETL website at: www.netl.doe.gov

Customer Service: 1-800-553-7681