Zero Discharge Water Management for

Horizontal Shale Gas Well Development

TECHNOLOGY STATUS ASSESSMENT

Submitted by:

West Virginia Water Research Institute

West Virginia University

PO Box 6064

Morgantown, WV 26506

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."

Current State of Technology

Summary of Existing Industry

Hydrofracturing technology teamed with horizontal drilling has facilitated exploitation of huge gas reserves in the Devonian Marcellus Formation of the Appalachian Basin. Existing technology uses fresh water mixed with chemicals and sand injected under high pressure to fracture (frac) the formation. Disposal of the water returned to the surface is then either hauled to an underground injection control (UIC) certified well for disposal, treated or processed through a municipal sewage treatment plant. Withdrawal or disposal may conflict with aquatic life, recreational, industrial, or domestic uses. Transportation, disposal or treatment of the frac return water (FRW) can be very expensive depending on well location and water contaminants.

Technologies/Tools Being Used

Treatment at a municipal sewage treatment plant is usually preceded by alum addition to precipitate barium and strontium. However, the sewage treatment process does not address the high sodium and chloride content of the FRW and this practice is being reevaluated. This is a costly alternative that will be less widely used in the future as small towns and cities find that the high salt concentrations are detrimental to their digesters[1]. The number of UIC wells is extremely limited in the region and, consequently, transportation costs are exorbitant. A third option is evaporation/crystallization. One such unit, operated by AOP Clearwater in Fairmont is near commissioning. Other units are under consideration. Tolls for this facility are reported to be around $140/1000 gallons while reverse osmosis costs range from $6 to $10/1000 gallons. These are large, capital intensive and fixed facilities so transportation to site is an added cost. In addition, reverse osmosis generates substantial volumes of reject disposal (up to 30%) that must be disposed.

The more cost-effective alternative is on-site treatment of the produced water to the degree needed for reuse as frac water. Recycling of produced water lowers transportation costs, environmental conflicts, and the risk of interruption in the well development schedule. In

order to be feasible, the returned frac water must be treated to a level where dissolved and suspended solids will not cause scaling in the injection train or clogging of pore space in the formation.

Benefits and Inadequacies of Current Technology

On-site treatment of produced water has been successfully accomplished using Reverse Osmosis (RO) as the primary treatment technology. However, extension of the RO technology to the treatment of flow back water from hydraulic fracture operations has required pre-treatment technologies designed to protect, and thereby extend, the life of the RO unit.

A consortium of oil producers and service companies, led by Texas A&M University, has developed a unique RO process that is specifically adapted to oilfield wastewater purification, which was licensed to GeoPure Water Technologies. The RO pilot system was extensively tested in the laboratory and field, and results show that dissolved solid levels up to 50,000 mg/L can be reduced to the level of fresh water. Extension of this technology to treating frac water returns required the RO unit to be protected to prevent early plugging of the membranes. Under a DOE contract, Texas A&M is evaluating pretreatment options that include combinations of liquid-liquid centrifuges, organoclay absorbents, microfiltration, and different oil resistant membrane materials and membrane types. GeoPure subsequently produced a 200-gpm unit incorporating some of the pretreatment options and used it successfully for about 9 months to treat Barnett Shale frac water of at least 13,400 mg/liter total dissolved solids[2]. The unit is not currently in use. These pretreatment technologies add to the cost of the unit, which may discourage producers to adopt on-site treatment of Marcellus Shale flowback using this approach.

ProChemTech invented a sequential precipitation process for treatment of flowback water. The first precipitation removes suspended solids, iron, and barium from the flowback waster as a solid, typically non-hazardous, sludge cake. The remaining scale formers (calcium, iron, magnesium, manganese, and strontium) are precipitated to make one solid sludge cake

which could be used as an alkaline soil amendment or for abandoned mine spoil reclamation. The process does not materially change the concentration of dissolved solids in the FRW. ProChem concludes that the only known alternative to their process is the GE Thermal Evaporation process which uses a vertical-tube evaporator to convert industrial wastewaters into distilled water for reuse[3].

Other companies have identified water treatment systems for solving the FRW problems, all based on existing technologies. Some prominent examples include a partnership between Devin Energy and Fountain Quail Water Management LLC (mobile vapor distillation @ $3.35 net per bbl), Ecosphere Technologies Inc. (Ozonix^{TM} mobile advanced membrane), and 212 Resources (thermal distillation and evaporation combined with polishing)[4].

Development Strategies

Why New Technology and Research is Required

Research is needed to clean the FRW to a point where it can be economically recycled. State-of-the-art technologies have not yet proven to be economically attractive to the haul and injection option. Development of more efficient pretreatment and filtration technologies can solve these problems.

Problems Being Addressed in this Research Project

The FilterSure technology offers a new approach ideally suited to remove suspended solids associated with the return of the frac water to the surface while promising an order of magnitude improvement in operating efficiency with associated lower costs. The technology is expected to replace all of the alternative pretreatment steps and, in so doing, dramatically reduce the costs and enhance the attractiveness of water re-use. This technology has the potential to anchor a recycle process that will compete with haulage and injection well disposal.

The key to the research is to remove enough of certain problem-causing constituents of the frac flow-back water such that they won't interfere with the subsequent frac job. This means that the frac water should have as few suspended solids as reasonably possible. Additionally,

certain dissolved solids must be reduced to low concentrations to eliminate the potential for forming “scale” compounds. After removal of multivalent metallic ions, the remaining dissolved solids such as sodium chloride, calcium chloride, magnesium chloride, and other salts may also need to be reduced. Because these chlorides are highly-soluble making them less likely to contribute to scale forming, and because they contribute to shale stability, moderate concentrations can be tolerated or even helpful. Water with total chloride content on the order of 25,000 ppm can readily be reused for a frac fluid base[5]**.** Higher chloride concentrations can be diluted with fresh make-up water to create an acceptable frac fluid base. If necessary, higher chloride concentrations may be removed by vacuum distillation, salt crystallization, electocoagulation, or membrane filtration. The FilterSure technology is being tested with other high potential technologies to develop a viable water clean-up approach.

Future

Barriers to be Overcome

The most difficult problem is to develop a cost-effective system to handle the broad spectrum of the suspended and dissolved materials preventing reuse of the FRW. These include heavy metals, natural hydrocarbons, water hardness, biological contaminants, and possibly radioactive contaminants.

FilterSure has already identified appropriate filter media for the system and is currently testing media sequence at the WVU laboratory located in Morgantown, WV. WVU is developing an effective complementary process for increasing the efficiency and effectiveness of the basic filter unit so that the effluent from the system can provide a high quality fluid for reuse in fracturing nearby gas wells. Laboratory work is currently underway with a target decision to proceed to construct and test a mobile unit late in 2010.

Impact on the U.S. Domestic Gas Supply Industry

The successful development of the FilterSure technology for clean-up and reuse of FRW will both improve economics and, at the same time, resolve environmental issues. Improved

economics will be achieved by reducing FRW trucking and disposal costs. By reusing the FRW for subsequent frac treatments, the need for new, fresh frac water for future wells will be reduced by 20% to 40%, depending on the amount of injected water that is returned after the frac. This will save costs by reduced freshwater hauling. Because the mobile unit will operate continuously with little or no need for an attendant, system operating costs also will be minimized.

Significant environmental benefits include the reduction in fresh water needed for future fractures, lowering the demand stress on local streams. Fewer trips with water trucks will cause less damage to local roads, create less fugitive dust emissions, create less engine exhaust, create less mud and muddy water, and create significant "good will" in the local community.

Deliverables (Tools, Methods, Instrumentation, Products)

Water treatment approaches have been identified and research is currently underway to evaluate each alternative for possible use in a mobile unit. Industry has provided water samples for testing with these samples covering the likely range of water that will need to be treated in field operations. Phase I will lead to a decision to proceed with the construction of a mobile unit. In Phase II, a 30-gpm mobile system will be constructed for testing at an active field drilling site.

---

[1] 2010. Pennsylvania Senate Environmental Resources and Energy Committee. Testimony on Marcellus Shale Wastewater Treatment Issues, 1/27/10.
[2] 2007. Geopure. News release/abstract, May, 2007
[3] Keister, Timothy. Marcellus Gas Well Water Supply and Wastewater Disposal, Treatment, and Recycle Technology. ProChemWhite Paper, following USPTO Patent application 61/199,588, Process for Treatment of Gas Well Completion, Fracture, and Production Wastewaters for Recycle, Discharge, and Resource Recovery, filed 11/19/08.
[4] 2008. Permian Basin Oil & Gas Magazine. The Future of Water Recycling. Issue No. 2 July 2008.
[5] Personal communication with BJ Services' Research Group, Houston,TX. 713-462-4239