Innovative Treatment of Shale Fracturing Flowback and Produced Water for Reuse or Discharge

B. Pakzadeh[1], B. Mastin[2], B. Chatterton[3], J. Renew[4], J. Wos[5], D. Philbrook[6], J. Min[7] and A. Chan[8]

[1]Southern Research Institute, Cartersville, GA, U.S.A., pakzadeh@southernresearch.org
[2]Southern Research Institute, Birmingham, AL, U.S.A., E-mail: mastin@southernresearch.org
[3]Southern Research Institute, Durham, NC, U.S.A., E-mail: chatterton@southernresearch.org
[4]Southern Research Institute, Cartersville, GA, U.S.A., E-mail: renew@southernresearch.org
[5]Southern Research Institute, Birmingham, AL, U.S.A., E-mail: wos@southernresearch.org
[6]M2 Water Treatment Inc., Raleigh, NC, U.S.A., E-mail: davephilbrook@m2wt.com
[7]BKT United, Anaheim, CA, U.S.A, E-mail: jhm@bkt21.com
[8]BKT United, Anaheim, CA, U.S.A, E-mail: ac@bkt21.com

ABSTRACT

Southern Research Institute, with project partners BKT United (Anaheim, CA) and M2 Water Treatment, Inc. (Raleigh, NC) received an award from Research Partnership to Secure Energy for America (RPSEA) to develop an innovative, cost effective, and robust approach for treatment of shale gas fracturing water that produces National Pollution Discharge Elimination System (NPDES) quality water for discharge and/or reuse. This approach combines and optimizes four technologies. Magnetic ballast clarification (MBC), vortex-generating nano-filtration (NF) membrane, and conventional reverse osmosis (RO) will be used to remove total suspended solids (TSS) and total dissolved solids (TDS), e.g., metals and naturally occurring radioactive materials (NORMS) from flowback and produced waters. Residues containing metals, NORMs, and/or trace elements will be managed with hydrogel adsorbent or precipitation / solidification / stablization.

Keywords: membrane, fracturing water, magnetic ballast clarification, solidification, hydrogel media

1 INTRODUCTION

As conventional gas reserves are declining, unconventional oil and gas production is increasing at a rapid rate and now accounts for approximately 46-percent of total United States (US) production [1]. Natural gas demand in the US is expected to rise by greater than 45-percent, from 22 trillion cubic feet (Tcf) in 1996 to between 32 and 37 Tcf in 2020. The significant increase in oil and natural gas production is expected to be possible due to advances in drilling technology that will allow for more efficient recovery of oil and gas from deposits.

Conventional gas extraction involves vertical and horizontal drilling operations which produce a variety of wastewater products (e.g., fracturing, produced, and flowback waters) that must be treated for reuse and/or disposal. Fracturing water requirements range from 3 to 5 million gallons in a horizontal well, approximately 10 to 30-percent released from the well as flowback water when the pressure is released. Flowback water flows out of the well over a period of about ten days followed by produced water, a mixture of water that was trapped underground with the oil or gas deposit and fracturing water, flowing out of the well with the oil or natural gas over the life of the well.

All wastewaters produced by drilling and fracturing are regulated by the Clean Water Act (CWA) and are subject to the technology-based regulations (40 CFR Part 435, Subpart C) which apply to onshore facilities “engaged in the production, field exploration, drilling, well completion and well treatment in the oil and gas extraction industry.” The effluent guidelines at 40 CFR 435, Subpart C establish best practicable control technology currently available (BPT) for onshore facilities and prohibits the discharge of wastewater pollutants into navigable waters from any source associated with production, field exploration, drilling, well completion and/or well treatment [2, 3]. The US Environmental Protection Agency (USEPA) also identified technologies that oil and gas producers may use to comply with the CWA including but not limited to deep-well injection and evaporation ponds. Wastewater produced during shale oil or gas extraction may also be discharged to publicly owned treatment works (POTW) provided that this wastewater does not interfere with the operation of the POTW or cause a violation of the POTW’s national pollutant discharge elimination system (NPDES) permit.

Large oil or natural gas producers are drilling new wells at such a rapid rate that they are reusing flowback and produced wastewater by blending it with freshwater 90:10

CTSI-Cleantech 2014, www.ct-si.org, ISBN 978-1-4822-5819-6

(freshwater to wastewater) and using it to fracture new wells. Some producers are at a disadvantage in that they do not bring on new wells at a rate high enough to reuse all their wastewater which subsequently requires treatment and thus increases operating costs compared to large producers. Recent dips in natural gas prices have slowed the rate of new well drilling, and thus will require producers to treat their wastewater.

The fluid used for fracking is composed of approximately 90-percent water, 9-percent sand to prop open the fissures produced by the fracking operation, and approximately 0.5-percent chemical additives including friction reducers, scale inhibitors, iron chelators and/or biocides. The wastewater from fracking and gas production typically contains high levels of total dissolved solids (TDS) (20,000 to 250,000 mg/L) hydrocarbons, metals, and total suspended solids (TSS) of 100 to 1,000 mg/L. Presence of these contaminants precludes the untreated reuse of this water for fracking (without blending with a minimum of 90% freshwater) or discharge onto land or directly to surface water. Discharge to a POTW is the most common method for handling flowback water, but transportation costs are extremely high and POTWs are limited regarding how much water they can accept and subsequently treat. For example, the Pennsylvania Department of Environmental Protection has restricted the amount of produced and flowback water which may be sent to POTWs in response to high TDS levels in the Monongahela River [4, 5]. This effectively halted gas drilling operations in some locations in western Pennsylvania.

A novel and cost effective method for treating natural gas wastewaters for disposal/reuse must be developed to maintain the environmental stewardship, preserve the favorable economics of gas shale development, and make it possible for producers to continue shale gas development. Magnetic ballast clarification (MBC) with vortex membranes and adsorbents or solidification/stabilization technology to produce clean water, low volume metals free brine, and a stabilized/non-hazardous solid waste is an innovative and promising technology integration that would significantly reduce the capital and operational costs of gas production.

Southern Research Institute (Southern Research) is developing an innovative, cost-effective, and robust approach for treatment of shale gas frac water to produce NPDES quality water for discharge and/or reuse. The approach comprises optimizing the combination of four technologies, two for frac water treatment and two for treatment and disposal of residues (i.e., high solid slurry and membrane concentrate) from the frac water treatment. The frac water treatment technologies are MBC for removal of TSS, metals, and naturally occurring radioactive materials (NORMs), and vortex-generating and nano-filtration membranes for removal of TSS and/or TDS. Residue treatment/disposal technologies are hydrogel adsorbent for metals, NORMs, and trace element removal, as well as precipitation, solidification and stabilization.

This paper presents the background and theory of the treatment processes used and provides an update on the latest developments of this project.

2 BACKGROUND

2.1 Magnetic Ballast Clarification

The MBC technology is a magnetic ballast system that performs solids separation from water efficiently and, when considering other clarification systems, is a comparatively small and integrated system. Reuse of the magnetite is critical to making MBC economically viable. MBC captures, cleans, and recovers the magnetite. Magnetic drums lift the magnetite/particle combination from the system, leaving most of the water behind. The magnetite is then mechanically sheared from the particles to be recovered. Magnetite and the sheared non-magnetic particles are then discharged onto another magnetic drum where the magnetite is recovered and returned into the unit.

Compared to conventional technologies, MBC technology requires a decreased physical space, and will allow for the development of a portable treatment system that may be more applicable to small producer applications. As previously noted, MBC can provide contaminated-water treatment levels comparable to conventional technologies, demonstrating its potential ability to replace both clarifiers and sand filters.

2.2 FMX Vortex Membrane Technology

FMX is a membrane filtration system which utilizes a vortex generated on the membrane surface to prevent fouling. The throughput from conventional membrane filtration systems (e.g., spiral wound) decreases due to the buildup of foulants on the membrane surface that form boundary layers. FMX's specially designed blades generate a strong Kármán Vortex which disrupts the accumulation of boundary layers. The Kármán Vortex is a strong swirling pattern caused by unsteady separation of flow over bluff bodies. A lightweight plastic that is resistant to chemicals and corrosion is utilized to build the bodies of the blades. This design concept allows a continuous turbulent flow to work efficiently on the membrane surface.

2.3 Hyrogel Adsorbent

Proposed technologies for managing membrane concentrate from the fracturing water treatment include hydrogel adsorbent and / or precipitation / solidification / stabilization. BKT's low-cost hydrogel adsorbent, produced from seaweed-extracted biopolymer and iron, can be used to adsorb metals, trace elements, and possibly NORMs from membrane concentrates [6, 7].

2.4 Precipitation, Solidification, and Stabilization

Southern Research will optimize a combination of chemical precipitation, solidification, and stabilization technology for application to MBC slurry and membrane concentrate.

Typically, metal bearing wastes are mixed with Portland cement, coal fly ash, bottom ash, and/or lime [8]. The following compounds are most likely to be formed in the process resulting from the hydration reaction of Portland cement, in which the metals would be trapped include: calcium silicate hydrate ($CaO.SiO_2.nH_20$), Ettringite hydrate ($3CaO.Al_2O_3.3CaSO_4.32H_2O$), and Monosulphate ($3CaO.Al_2O_3.CaSO_4.12H_2O$) [8]. For the proposed application, an optimized recipe would be developed. Since Portland cement is expensive, the use of fly ash or bottom ash may be preferable. The produced waste must pass toxic characteristic leaching procedure (TCLP) evaluation and also provide an unconfined compressive strength of 50 PSI in order to dispose of the residuals in conventional landfills.

3 EXPERIMENTAL DESIGN

A field sampling and analysis plan, sampling protocols, and management of hazardous waste were developed. Measurements will be conducted using EPA compliant methods according to the standard methods for the examination of water and wastewater or other approved methods [9].

3.1 Technology Integration

Efficacy of three process integrations will be evaluated in the laboratory. An integration that demonstrates the best potential will be demonstrated with a pilot-scale field demonstration. For each water sample, simulation experiments will be performed to identify:

- Polymer(s) and chemical(s) to remove solids, metals and NORMS with the smallest chemical dosages and corresponding magnetite usage, as well as greatest recovery in the MBC.
- Membrane type (e.g., manufacturer and model) and pore size (e.g., UF, MF, or NF) required for maximum suspended or dissolved solids removal in the FMX Vortex-Generating Membrane and Conventional Reverse Osmosis (RO) Systems. A comparison of membrane results in the lowest resistance (highest flux) and highest rejection of target contaminants.
- Type and mass of adsorbent (i.e., Hydrogel Media) which removes the highest metal concentrations from resulting membrane concentrates.
- Functional protocols for treatment of slurry and membrane concentrates with chemical precipitation, solidification and/or stabilization.

Efficacy data will include characteristics of the influent flow back / produced water including but not limited to suspended solids, oil and grease, 5-d biological oxygen demand (BOD5), chemical oxygen demand (COD), metals, and NORMs, dissolved solids removal efficiencies, mass of removed solids, characteristics of the generated slurry and brine, required treatment chemicals, chemical(s) doses, costs, and potential to recycle magnetite. Figure 1 presents a process integration in which oil is separated in an oil separator, suspended solids, bacteria and other organic are separated in the MBC clarifier, and the dissolved solids and NORMS are separated within the membrane process.

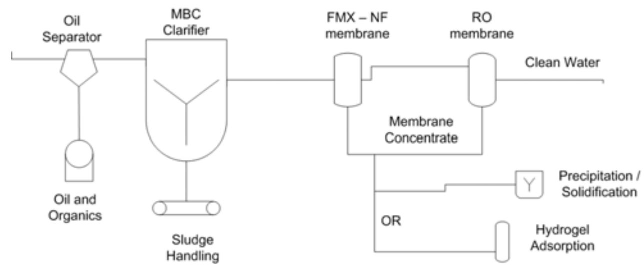

Figure 1: Example of schematic process integration.

4 RESULTS AND DISSCUSSION

Recent results from a bench-scale test of MBC to treat produced water from Bakken Shale demonstrated excellent suspended solids and iron removal. The treatment data in Table 1 includes removal of materials from produced water from benchtop MBC simulations.

Application	Parameter	Untreated	MBC (Treated)	% Removal
Produced Water (Bakken Shale)	Turbidity (NTU)	417	32.7	92.2
	Silica (mg/L)	41.7	6.5	84.4
	Total Iron (mg/L)	157	7.2	95.4

Table 1: MBC Performance Data.

Recent results from a bench-scale test with a FMX treatment system followed by spiral wound RO to treat produced water from Bakken Shale demonstrated excellent rejection of sulfate while maintaining good flow, achieving up to 90% water recovery. Poor performance of the system for high TDS, produced water from Marcellus was observed in comparison to excellent flow and good rejection of multivalent ions for produced water from Fayetteville Shale. The preliminary data may have been attributed to different membranes tested at each site, and as such further research is needed to optimize the system for these high TDS produced waters [10]. An example of the above mentioned study for the produced water with NF is presented in Table 2.

Application	Parameter	Untreated	FMX Treated	% Removal
Produced Water (with NF)	Calcium (mg/L)	330	140	57.6
	Magnesium (mg/L)	76	11	85.5
	Strontium (mg/L)	110	33	70
	Silica (mg/L)	5.3	4.4	17
	Sodium (mg/L)	4,400	3,300	25

Table 2: FMX Performance Data from Bakken Shale.

5 CONCLUSIONS

The primary objective of this research is to analyze four proposed technologies to determine the most cost effective and efficient integration to handle fracturing, flowback, and produced water and discharge NPDES quality effluent. The proposed research evaluates MBC technology which includes mixing a magnetite ballast, flocculant and water to form magnetic floc, and agitating the magnetic floc in a flocculation zone. Ultimately, the magnetite ballast will be separated and reused. FMX is a new anti-fouling membrane system based on the simple, yet innovative concept of using vortices to prevent fouling of the membrane for high density, high viscosity, and high solid applications. Hydrogel media is a single-use adsorption media providing a simple approach for brine treatment and volume reduction. Solidification/stabilization (S/S) with fly ash, cement, and/or other chemicals will be applied to brine, solid waste, sludge, and/or residuals in order to immobilize metals. Various technology integrations may be required due to variability in produced water characteristics across domestic gas and oil shale plays.

This project will allow for the development of this technology through use of public funds, thereby reducing the financial risk to small producers of funding novel technology research and development. Through development of a less expensive approach to fracturing water treatment, economic viability of producers, and environmental stewardship of fracking operations are more likely to be achieved and negative environmental impacts (i.e., freshwater use, wastewater discharges, and solids disposal) are likely to be reduced at local levels.

6 AKNOWLEDGEMENT

Funding from the Research Partnership to Secure Energy for America (RPSEA) and project guidance and assistance from Kent Perry of RPSEA are acknowledged.

REFERENCES

[1] Institute for Energy Research (2011). "North American Energy Inventory." Washington, DC, Available online: http://www.energyforamerica.org/wp-content/uploads/2012/06/Energy-InventoryFINAL.pdf

[2] Veil, J. A., Puder, M. G., Elcock, D., & Redweik Jr, R. J. (2004). A white paper describing produced water from production of crude oil, natural gas, and coal bed methane. ANL Report under DOE (NETL) Contract W-31-109-Eng-38.

[3] Honker, W. K., & Director, A. Authorization to Discharge Under the National Pollutant Discharge Elimination System.

[4] Andrews, A. (2009). Unconventional gas shales: development, technology, and policy issues. Diane Publishing.

[5] Wilson, J. M., & VanBriesen, J. M. (2012). Oil and gas produced water management and surface drinking water sources in Pennsylvania.Environmental Practice, 14(04), 288-300.

[6] Min, J.H., Boulos, L, Brown, J., Le Gouellec Y., Cornwell, D., Coppola, E., Baxley, S., Rine, J., Hering, J., Vural, N. (2005). "Innovative Alternatives to Minimize Arsenic, Perchlorate, and Nitrate Residuals". AwwaRF Final Report, March.

[7] Min, J.H. and Hering, J.G. (1998). "Arsenate, Selenite, and Chromate Sorption by Fe(III)-Doped Alginate Gels." Advances in Environmental Research, 2: (2):207-217.

[8] Quian, G., Y. Cao, P. Chui, and J. Tay. (2006). "Utilization of MSWI Fly Ash for Stabilization/Solidification of Industrial Waste Sludge." Journal of Hazardous Materials, B129, 274-281.

[9] APHA, AWWA, and WEF, (2012). "Standard Methods for the Examination of Water and Wastewater", 22nd ed, American Public Health Association, Washington, DC.

[10] Keizer, T.S., Burney, J.R., Limke, J.C., Min, J.H., Eum, Y.J., (2012). "Opportunities for Treatment and Reuse of Acid Mine Drainage and Produced Water in Oil and Gas Shale", International Water Conference, San Antonio, Texas, November.