



MARCELLUS SHALE – WATER TREATMENT OPTIONS WORTH CONSIDERING

Centered in western Pennsylvania, the Marcellus stretches over some 600 miles of the Appalachian Basin from West Virginia and northeast into the state of New York. Marcellus has been estimated to contain anywhere from 168 trillion to 516 trillion cubic feet of gas. A member of the Devonian black shales, Marcellus is categorized as a dual porosity reservoir, wherein fractures can be drained rapidly while the shale matrix is drained more slowly. According to geologists, the matrix holds much of the gas, so it's vital to connect the matrix porosity to the wellbore for the most productive completions.

Gas exploration today not only requires better reservoir knowledge and superior drilling methods, but also highly targeted completion technologies. Our customers want to improve their use of precious water assets to support not only multi-stage fracturing, but also well completion efficiencies and improved water conservation.

A gallon of water involved in fracking has an interesting journey. First it receives a mixture of chemical additives: a friction reducer (a polymer to reduce the viscosity of the water and improve its flowability so it's easier to pump down the well), a special grade of light sand, and a cross-linked guar gel that helps to carry the sand down into the well. This fracking fluid is injected into a gas hole at a high flow rate and pressure to break up the formation, increasing the permeability of the rock and helping the gas flow toward the surface. As the water cracks the rock formation, it deposits the sand. As the fractures try to close, the sand keeps them propped open. Fracking typically occurs once when a well is newly drilled, and again after a couple of years when the rate of gas flow begins to decline.

Underground, the fracking fluid picks up other contaminants present in the rock formation, including barium, calcium bicarbonate, iron, magnesium sulfate, sodium chloride, and strontium.

Each gas well in the Marcellus Shale uses two- to four- million gallons of water for drilling and fracturing and even more if the well must be re-fractured.

As little as 25 percent and as much as 100 percent of the fracture water returns to the surface. This water, often referred to as flow-back water, contains hydrocarbons, salts, dissolved solids, etc. The first flow-back water has a salt content of only between 1,500 and 2,000 parts per million, but the longer the water remains in the Marcellus Shale, the saltier it becomes. By the end of the first week, the salt content can reach 45,000 parts per million. Sea water averages between 10,000 and 35,000 parts per million. The high salt content makes the water highly corrosive to metals and harmful to land, vegetation, and other living organisms.

Some water continues to flow out of gas wells once they are in production. This water is referred to as produced water. Some wells may indeed have more produced water than flowback water.

A typical Marcellus well development will involve approximately 30,000 barrels (1.26 MG) of flowback. The present philosophy is to send this flowback, as well as produced water to off-site treatment and disposal that may be many, many miles away, requiring a fleet of some 300 vehicles to haul the flowback water to an acceptable treatment facility. Furthermore, the current off-site treatment and disposal capacity in Western Pennsylvania is severely lacking. Furthermore, in May of 2008, the PA DEP sent formal letters to all of the publically owned treatment works (POTWs) explicitly outlining that they were prohibited from taking this waste stream without a rigorous permitting step, if at all.

Under current off-site disposal philosophy, this flowback water is not recycled. Millions of gallons of natural water resources are lost. For every well, the estimated 300 transport trucks will also release an estimated 40 tons of CO₂ emissions into the environment. These transport trucks make hundreds of round trips a day, congesting traffic flow in the surrounding community and deteriorating roads and highways. In addition, at the current price of diesel, significant cost impact is realized via this current philosophy. Off-site treatment is estimated to cost between \$0.03 and \$0.05 per gallon.

The solution to off-site disposal is on-site treatment and reuse. An estimated 50% - 60% total savings can be realized by treating and reusing flowback and produced water on-site. There are a number of on-site treatment options worth considering including evaporation/crystallization, advanced oxidation, membrane filtration, etc. A few of these technologies are discussed in more detail below.

At Venture, we are working with our clients to determine the most economically viable treatment option for each site. Site factors such as available power and final water quality are often the determinant in treatment selection. After determining the most economical on-site treatment solution, Venture designs (using 3D AutoCAD Inventor) mobile skids that can be deployed

directly to the well-site to improve water recovery, reduce environmental impact, eliminate hauling costs, and drastically reduce off-site treatment costs. Further, because the treatment and recycle plant is mobile, it can be moved and reused at multiple well sites, and requires far less time to permit and install (since it is not a permanent facility).

On-site treatment technologies have proven capable of recovering between 70% - 80% of the initial water to potable water standards and made immediately available for reuse in the frac process. The remaining 20% - 25% is very brackish and considered brine water. In addition produced water has even higher salt concentrations than flowback. Some technologies can further treat the brine water, increasing recoverability by as much as 24%. In most cases, this recovered brine water cannot achieve potable water standards, but can sufficiently be cleaned for other on-site or off-site uses as 'process water'. In other cases, the brine water is simply sent for off-site treatment and disposal. The economics here are primarily distance from a treatment facility with available capacity to undertake your development.

On-Site Flowback/Produced Water Treatment Alternatives

Advanced Oxidation Process

The advanced oxidation process (AOP) is successfully used to decompose many hazardous chemical compounds to acceptable levels, without producing additional hazardous by-products or sludge which require further handling. The term advanced oxidation processes refers specifically to processes in which oxidation of organic contaminants occurs primarily through reactions with hydroxyl radicals. AOPs usually refer to a specific subset of processes that involve O₃, H₂O₂, and/or UV light. The most widely applied advanced oxidation processes (AOP) have been:

- Peroxide/ultraviolet light (H₂O₂/UV),
- Ozone/ultraviolet light (O₃/UV),
- Hydrogen peroxide/ozone (H₂O₂/O₃)
- Hydrogen peroxide/ozone/ultraviolet (H₂O₂/O₃/UV) processes.
- Ozone/Ultrasonic cavitation
- Advantages of Advanced Oxidation Processes
- Rapid reaction rates
- Small foot print
- Potential to reduce toxicity and possibly complete mineralization of organics treated

Technical Brief

- Does not concentrate waste for further treatment with methods such as membranes
- Does not produce materials that require further treatment such as "spent carbon" from activated carbon adsorption
- Non selective pathway allows for the treatment of multiple organics at once

Disadvantages of Advanced Oxidation Processes

- Capital Intensive
- Complex chemistry must be tailored to specific application
- For some applications quenching of excess peroxide is required

Mechanical Vapor Recompressor Evaporation/Crystallization

A vapor-compression evaporator, like most evaporators can make reasonably clean water from any water source. In a salt crystallizer, for example, a typical analysis of the resulting condensate shows a typical content of residual salt not higher than 50 ppm or, in a different concept, not higher than 10 $\mu\text{S/cm}$. This results in a drinkable water, if the other sanitary requirements are fulfilled.

For economic reasons evaporators are seldom operated on low-TDS water sources. Those applications are filled by reverse osmosis or membranes. However, vapor compression chiefly differs from these thanks to its ability to make clean water from saturated or even crystallizing brines with total dissolved solids (TDS) up to 650,000 mg/L. Membranes and RO systems can make clean water from sources no higher in TDS than approximately 35,000 mg/L.

A mechanical vapor recompression evaporator system is similar to a conventional steam heated, single-effect evaporator, except that the vapor released from the boiling solution is compressed in a mechanical compressor. Compression raises the pressure and saturation temperature of the vapor so that it may be returned to the evaporator steam chest to be used as heating steam. The latent heat of the vapor is used to evaporate more water instead of being rejected to cooling water in a condenser. The compressor provides energy to the vapor that increases in pressure and temperature, thereby recycling the evaporated water into usable steam to meet the evaporative load of the incoming fluid. This reduces the steam needed to meet the evaporative load of the overall system. The energy or driving force for pressure increase is provided through shaft horsepower.

Furthermore, the MVR process is very efficient because of the heat recovery. For example if you boil water on a stove, producing one pound of steam takes approximately 1000 BTUs. Because

of heat recovery, an MVR can produce one pound of steam with 25 to 40 BTUs per pound, or about 1/40th of the energy required to boil water on the stove.

In order to maximize the investment in on-site treatment technologies, a mobile solution is necessary. Mobile MVR's are possible within the footprint of a traditional MVR evaporator—about 2,500 square feet. Because the units can be skid-mounted and designed for highway transport on low-boy trailers, they don't require special permitting and can easily be moved from well to well.

All that is needed in addition to the process skids are interconnecting pipes and electrical connections, and a spark-ignited, 50-kW generator set. This type of set-up would eliminate the need for any external source of electric power, as natural gas, drawn directly from the well, is used to operate the compressor and to drive the generator, which produces electricity to power the pumps, instruments, and controls.

When treatment at one site is finished, the operators can drain the system, load it on the trucks with a crane, haul it to a new site, and have it set up within a couple of days.

Summary

There are a number of challenges facing development of the Marcellus shale gas, including siting, permitting, drilling challenges, access to pipelines, etc. However, water acquisition and disposition should not be one of them.

At Venture, we are confident that an on-site treatment facility similar to one of the above would save significant time and money for any development. Because Venture Engineering is not an equipment supplier/dealer, we have the ability to look at each development with an unbiased opinion on technology. We evaluate each site and match the technology the best fits the situation, even, in some cases, if that means that off-site treatment is indeed the least cost alternative.

For more information on Venture Engineering's process engineering capabilities, please contact Travis Buggy at 412-231-5890, ext. 325. Or visit us on the web at www.ventureenr.com.

Dave Moniot has over 19 years experience Mr. Moniot has over 19 years of experience in the management, coordination, and execution of chemical, energy (including cogen and CHP), petrochemical, refinery, pharmaceutical, healthcare and research and development projects, and metals. He holds a Bachelor chemical engineering degree from the University of Pittsburgh. He can be reached at (412) 231-5890 x301, or at dmoniot@ventureenr.com.