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"Game Changing Technology for Treating and Recycling Frac Water"

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Abstract

This paper addresses an advanced oxidation and precipitation water treatment process employed as an on-the-fly fluid pretreatment during hydraulic fracturing operations. The water treatment technology will allow for substantial reuse of flowback and produced fluid while at the same time completely replacing liquid biocide and scale inhibitor fluid treatment during fracs. Additionally, the treatment process generates zero waste. To date, the technology has been used on hundreds of wells successfully treating over 17 million barrels. The paper will report on more than 2 years of field operations on hundreds of frac stimulations as well as numerous pilot operations in multiple shale plays. Dynamic tube-blocking tests show that the treated fluid will not deposit scale even after days of storage in an open frac tank. Field sample testing shows the injected brine has 3 to 6 log-cycle kill of sulfate-reducing and acid-producing bacteria populations. With the move toward environmentally safe chemicals, an economical process eliminating chemicals is a step forward for our industry. The equipment is purposely designed to segue directly into the fracturing process without interfering with service company pumping operations or having any compatibility problems with any service company products. Our paper will show definitive results from field operations of an economic water treatment system that will allow for a reduction in liquid chemical usage and closed-loop management of wastewater. The newest design would treat 80 barrels per minute, occupying a footprint roughly the size of a frac tank. The units can be deployed in tandem for higher flow rate requirements.

Introduction

The company that developed the Advanced Oxidation and Precipitation Process (AOPP) reported in this paper was previously involved in stripping paint from ship hulls in dry-dock. The process involved extremely high-pressure water applied using a robotic vehicle that moved up and down the ship's hull using 40,000 pounds per square inch (psi) water pressure. One of the major challenges associated with this project was dealing with the toxic paint and other extraneous material removed from the ship's hull. In 2003, the Environmental Protection Agency successfully tested a water treatment system designed by the company to neutralize or remove contaminants from wastewater generated during decontamination activities following a biological or chemical terrorist attack. Further research and development led to the patented advanced oxidation and precipitation process, which the company incorporated in equipment specifically designed for the oil and gas industry. The equipment has largely been used in Arkansas and Oklahoma with pilot work done in Texas and Louisiana. To date, seventeen million barrels of oilfield water have been treated using the process without any adverse reaction.

The initial concept was to clean fracture flowback fluid to a quality that would allow the economic removal of salinity using reverse osmosis for the purpose of surface discharge. The Oklahoma Corporation Commission witnessed the process and approved a permit to treat flowback fluid for surface discharge for land farming applications. During this process management decided to focus its efforts on the disinfecting and scale inhibiting benefits of the proprietary AOPP pretreatment. Since the technology is scalable, it was integrated into frac tanks on the front side of fracture stimulations, thereby replacing liquid biocides and scale inhibitors. Because of the efficacy of the system at high rates with challenging fluids, operators could treat flowback and produced fluid on location on-the-fly, thereby eliminating the need for an offsite treatment location. Operators are using this process to frac with mixtures of surface water, ground water, flowback and produced fluid. We will document successful bacteria treatment and scale inhibition from these operations.

This process could not have come at a better time given the political discussions about hydraulic fracturing. The documentary *Gasland*, regardless of its deviations from truthfulness, alarmed citizens and brought great pressure to bear on the use of chemicals in the hydraulic fracturing process. We must address not only the need to eliminate chemicals but also the usage of large volumes of water required in the stimulation of shale and tight reservoirs. The AOPP described in our paper brings answers to both objections: the elimination of chemicals and the complete recycling of all the water.

Equipment Description

The treatment system is an advanced oxidation and precipitation process that uses ozone, hydrodynamic cavitation, acoustic cavitation, and electro-oxidation chemistry to provide microbial control and scale inhibition. The newest design consists of an AOPP unit that processes fluid at up to 80 barrels per minute (bpm). For frac jobs where the maximum treatment rate exceeds 80 bpm, two units may be used in tandem. A generator contained in the front of each unit provides electrical power. Water enters the system through two 10” pipes traveling thru static mixers that both homogenize the water and initiate hydrodynamic cavitation. Extremely high temperatures and pressures from bubble collapse cause thermochemical decomposition and produce highly reactive hydroxyl radicals. Hydroxyl radicals are reactive electrophiles that readily react with most organic compounds by undergoing addition reactions with double bonds or extracting hydrogen atoms from organic compounds. After passing through a mesh screen, water is moved by eight pumps each capable of moving 10 barrels per minute. These pumps are controlled automatically depending on water treatment rate requirements.

Ozone, created in the system using oxygen separators and plasma block ozone generators, is then injected into the fluid. Ozone is a highly reactive oxidant that kills bacteria and oxidizes heavy metals. In a controlled environment ozone is an extremely safe oxidant with which to work. The highly ozonated water then enters flash reactors that enhance ozone mass transfer efficiency in the water just before it enters the main system reactor. Ozonated water enters radially into the reactor at multiple points. Ultrasonic transducers create cavitation, again generating thermochemical decomposition and hydroxyl radicals. The passage of electricity through the water is the primary driver in precipitating hardness salts in the fluid. Ultrasound breaks apart the precipitated salts into nano-sized suspended particles that will not cause scale. The electrical field also reacts with oxygen in the water to create more hydroxyl radicals, which assist in further oxidation of bacteria. The total transit time of water through the system is approximately one minute. Field tests indicate the process also enhances the “slicking” of frac fluids, possibly reducing required pumping pressures.

The water leaves the reactor traveling through another large section of static mixers and electrodes to further augment treatment. The water, now free of bacteria and scaling tendencies, is pumped out of the system, ready for use. The process creates zero waste. Instead of providing separation of multivalent cations and troublesome anions like sulfate and carbonate, the AOPP precipitates these dissolved solids into suspended solids and all of the matter is pumped downhole.

Competing Technologies

We will outline competing technologies in two broad categories: offsite and onsite treatment. Offsite treatment includes any treatment that requires staging of water and equipment somewhere other than the location where it will be used as completion fluid. Onsite treatment occurs on location just prior to or during fracturing operations. Treatment technologies may also be grouped by the science driving the treatment. There are three broad categories into which treatment solutions may be grouped: Group I - Thermal Technologies, Group II - Physical Filtration and Group III - Chemical Treatments. Many treatments combine one or more of the three in one treatment package. Figure 1 shows an illustration of this grouping where some technologies fall in one discrete category and others fall in the overlap of two or all three types of treatment.

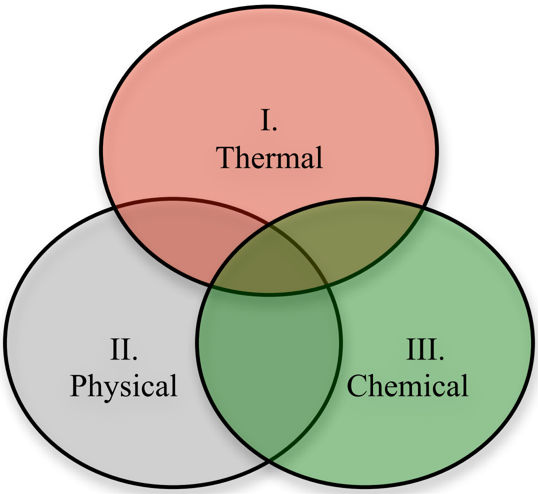

Figure 1: Water Treatment Categories

Onsite Versus Offsite Treatment

Onsite technologies provide sufficient treatment of recycled fluids to avoid adding another location where water will be treated. In order to treat during the frac, the technology must provide sufficient treatment rate to keep up with pumping rates. Onsite technologies, as it relates to this paper, will only have application for recycling fluids as long as there are new wells being drilled and fractured. There are few technologies that can treat fluid at hydraulic fracturing pumping rates and achieve successful treatment.

There is a broader technology offering in offsite technologies due to less restriction on treatment rate and footprint. Because fluid storage is more practical at offsite locations, operators can manage logistics such that there is just enough storage at the offsite location to support fracturing operations on an ongoing basis. Water is brought to the facility, treated and given back to operators to use as completion fluid. The waste from the facility is disposed separately.

Treatment Technologies - Group I - Thermal Treatment

Thermal treatment is provided by the water treatment industry in a few different forms. At their core, all are some energy-conserving derivative of evaporation, distillation and crystallization. There are no thermal treatments that could be classified as onsite, on-the-fly treatment technologies due to rate and footprint limitations.

Two benefits of thermal treatment are the flexibility and finality of the solution. The flexibility in that it works on any type of water, though the economics worsen as the quality of water worsens. For instance, reverse osmosis (one alternative to thermal treatment for creating fresh water from brine) only works on water with salinity less than approximately 40,000 milligrams per liter (mg/l). Thermal treatment will work on, for instance, Marcellus shale produced fluid with salinity greater than 200,000 mg/l. Another benefit of thermal treatment is the finality of the solution. Certain chemical treatments discussed later remove only selective scale-causing constituents, whereas thermal treatment removes virtually all dissolved and suspended solids from the fluid, rendering an effluent of unquestionable quality.

The downsides of thermal treatment are flow rates and cost. It’s difficult to achieve high flow rates in a small footprint and it is costly to generate enough energy to create water vapor from flowback and produced fluids. Even the most recent advancements in thermal technology do not allow for flow rates that could keep up with a fracturing stimulation. Also, the economics associated with the recycling of fluid for fracs do not, in most areas, support thermal treatment as a solution.

On the other hand, thermal treatment will have to be a part of the long-term solution. Treatment for reuse is only applicable if there are ongoing fracs. At some point in the development of a regional area, the supply of produced fluid will outstrip the fluid volume demand for fracs. In that case, the water will have to either be recycled to the environment or disposed via saltwater disposal wells. In areas where disposal wells are not available, recycling to the environment will make the most sense. Thermal treatment is a viable solution for discharging fluid back into the environment.

Treatment Technologies - Group II - Physical Treatment

Physical treatment includes a wide spectrum of technologies that remove different sized solids from water using a physical media. There are two subcategories of physical treatment: particle filtration for removing rocks and large suspended solids down to the size of about 0.5 microns; and reverse osmosis membranes that remove ions, to include chlorides. There are no physical separation treatments, or combinations thereof, that could provide suitable fluid treatment quality at a sufficient rate to maintain on-the-fly treatment without also adding a chemical treatment.

Although particulate filtration is important, we will focus this discussion on membrane treatment. Ultrafiltration is capable of removing molecular-sized particles such as colloidal silica. Nanofiltration is capable of removing multivalent cations such as iron, calcium and barium. Reverse osmosis is capable of removing virtually any ion, to include chlorides. Reverse osmosis may be employed with influent waters less than approximately 40,000 mg/l of total suspended solids. The repercussion of this limitation as it pertains to shale gas water management is that reverse osmosis is not a practical treatment for produced fluid, but only for flowback fluid from wells that have been fractured with low-salinity fluid.

The economics of reverse osmosis (RO) in treating flowback fluid comes down to the quality of the RO pretreatment and the recovery rate to which that translates. The pretreatment can consist of multiple combinations of chemical and physical pretreatments, all contributing to increased recovery rates and membrane life. If recovery is hovering around 50%, meaning that only 50% of the fluid that enters the membranes is product water, or fresh water, and 50% is reject fluid, or concentrated brine, then the economics become difficult. In addition, if RO membranes have to be replaced every few days or weeks in order to keep those recovery rates high, then the economics of the operation quickly spiral out of control.

The benefit of RO membranes is the extensive foundation of knowledge relating to their use. RO membranes are used all over the world in treating seawater. However, most RO treatments are high capital cost, low operating cost ventures, where footprint is not an issue and the influent is relatively consistent. Footprint and mobility aren’t as much of an issue with offsite treatment facilities in the oilfield, as long as they are strategically located in the field. However, oilfield wastewater is not consistent, and the pretreatment setup for an oilfield wastewater RO treatment system would reflect that need for flexibility, which would translate to capital cost in the facility.

Treatment Technologies - Groups III - Chemical Treatment

Group III includes any liquid chemical or oxidation treatments, and there are many. For the purposes of this paper, we will focus on two separate subcategories: 1) liquid chemical treatments and 2) oxidative and electrochemical processes.

Liquid chemical treatment existed in the oilfield long before the discussion of recycling fluids for fracs came about. It is an industry-accepted standard to treat completion fluids with biocide and in many cases scale inhibitor, even when the water being treated is relatively clean to begin with. As flowback fluids and produced fluids are recycled, many are exploring how to use this water with chemical treatment on location on-the-fly. There are also offsite facilities where chemical treatments are used to adjust pH, manage bacteria loads and separate constituents that could cause issues during a frac. Although chemical treatments at offsite facilities are relevant solutions, they are often combined there with physical separation and/or thermal treatment. The focus of this paper will be on their utilization as a sole treatment method onsite on-the-fly for recycling fluid for fracs.

Several operators in the Marcellus have successfully employed chemical treatment packages to recycle flowback fluid in the Marcellus. One operator teamed with a chemical company to frac a vertical Marcellus well using recycled fluid. The chemical treatment consisted of a salt tolerant friction reducer, a scale inhibitor, an iron agent and a biocide.

The cost for chemical treatment on location has generally been reasonable and, quite frankly, an afterthought for operators. It was cheap insurance to prevent bacteria growth and scale deposition in the relatively fresh waters predominantly used for fracs. Now, with the push to recycle flowback and produced fluid, the cost of these chemical cocktails will increase. Because chemicals can be used anywhere water is stored, chemical treatment is mobile. However, on-the-fly treatment is challenging due to the difficulty in blending the chemicals sufficiently with the fluid to obtain acceptable results. In addition, most chemical cocktails have to be tailored to a specific influent quality. For example, the chemicals required to inhibit calcium carbonate scale differ from those used to inhibit barium sulfate scale. A changing influent compromises effective treatment.

Adding liquid chemicals to completion fluids does not assist the industry in its political struggle to clear hydraulic fracturing as a safe, viable process for extracting oil and gas. The most practical concern in dealing with chemicals is that they must all be transported from Point A to Point B and they have to be handled at some point by people. In addition, if they are liquid, they can be spilled into the environment. Treatment designs using electricity and gases eliminate the possibility for spills; although exposure to gases and safety in dealing with electricity provide health and safety concerns that have to be mitigated.

Chlorine dioxide is one type of treatment that is generated on location from the combination of benign chemicals. It acts as a highly reactive free radical in water and is effective in oxidizing bacteria, hydrocarbon chains, hydrogen sulfide and iron sulfide. There are explosion dangers in handling the gas, although the industry is working hard to make these operations safer. Chlorine dioxide solutions have been deployed to field operations in the oilfield.

Ultraviolet treatment (UV) is another liquid-chemical free technology that has been fielded in hydraulic fracturing operations. Since UV involves the treatment of fluid with light, it stands to reason that the fluid must have low levels of turbidity in order to achieve effective treatment. Therefore, water treated via UV must be filtered effectively prior to UV treatment. This presents a potential problem in the oilfield where murky pond water is commonly used as frac fluid and achieving any real clarity via filtration at hydraulic fracturing treatment rates is difficult.

Neither chlorine dioxide nor ultraviolet treatment provide effective treatment for scale inhibition, so in order to prevent scale, the operator would still need to explore a liquid scale inhibitor treatment program.

Advanced Oxidation and Precipitation Process (AOPP) Operational Experience With Offsite Treatment

The AOPP was first used in December 2008 in the Woodford Shale in Southern Oklahoma to treat challenging produced fluid. The objective for treatment in this case was to re-use the produced fluid on subsequent fracs. The AOPP system there has been used to treat over 1,000,000 bbl of produced fluid, which has been used on over 200 completed wells. The produced fluid, in this case, is typically 170,000 mg/l total dissolved solids (TDS) and high in suspended solids. The primary treatment goal for the initial application in the Woodford Shale was to eliminate the scaling and corrosive effects of high TDS waters. The treated produced fluid then acted as a clay-stabilizing agent in the frac fluid matrix to prevent clay swelling or movement. The operator was using potassium chloride as a clay stabilizer prior to implementing the AOPP, but found that treating and reusing produced fluid for clay stabilization was more economical and efficient.

The operator positioned the AOPP system on location with a saltwater disposal well centrally located in the play. Whatever fluid not treated for reuse is disposed via the injection well. Vacuum trucks bring water to the facility and unload into a series of polyethylene tanks, which provide storage as well as settling for any residual liquid hydrocarbons. The produced fluid is treated through the AOPP system and discharged to a battery of frac tanks where it awaits transport to the next frac.

For offsite treatment, the AOPP system is incorporated with some solids filtration. This additional treatment allows for more residence time and works on more challenging water, but does create a small waste stream. The byproduct ends up being less than one percent of the total volume processed and is disposed via the disposal well onsite.

In some cases, the expense of operating an offsite facility, the additional trucking costs, and the waste stream developed from the process make this operational scenario less attractive to operators. It was these fallacies that contributed to the development of onsite, on-the-fly treatment of all waters during the fracturing process.

Advanced Oxidation and Precipitation Process (AOPP) Operational Experience With Onsite Treatment

An operator in a major shale play has used the AOPP on its fracs to treat the entire frac fluid volume. In this case the AOPP system treats at much higher rates on-the-fly on location. The AOPP has been employed in this manner since November 2009 on over 130 completed wells. The systems have treated over 16,000,000 bbl of frac fluid. For this application the AOPP was incorporated into a traditional frac tank. The frac tank was specifically designed so that the last 10 feet of the tank could be made into a compartment to house the AOPP equipment, including a power generator. The tank was built slightly taller so that it maintained a storage capacity of approximately 500 bbl. Each of these frac tank AOPP systems can treat at a rate of 10-20 bbl per minute. If the frac design calls for a pumping rate of up to 100 bbl per minute, then the treatment service provider would need 5 – 10 systems on location.

For this application, the frac tank based AOPP systems are rigged up on location as would a series of frac tanks for the purpose of storing fluid prior to entering the pumping company's manifold, blender, hydration unit, or booster pump. The operator prefers to bring all of the ground water, flowback fluid, and/or produced fluid to be recycled to the frac location. These reclaimed waters are stored on location in a lined pit. The water transfer company rigs up to the fresh water source as well as the reclamation pit. The operating company designs each job based on the quality of reclaimed water, amount of fresh water available, and reservoir characteristics. The operator provides the water transfer company with a detailed plan for each stage, which specifies the percentage of reclamation water to be used. The specified mix of fresh water and reclamation water is pumped to a specially designed manifold used to effectively mix the water prior to being distributed evenly to the AOPP frac tanks.

Each AOPP frac tank used for this project contains an on-board generator that powers the entire system. The process begins with an air compressor, which feeds an oxygen separator system. The pure oxygen is fed to several ozone generators that create ozone. The ozone is fed into the water stream via a venturi nozzle prior to the water entering mixing tubes and the AOPP reactor. The AOPP reactor contains the ultrasonic transducers used to bombard the fluid with ultrasound, which creates acoustic cavitation, and electrodes, which release electricity into the fluid to facilitate the electro-chemical precipitation of hardness salts. Treated water is dumped into the frac tank. The system contains an onboard pump used to recirculate the fluid from within the frac tank. The outlet connections from each AOPP frac tank are connected to a common 8" manifold. The pumping company rigs up their suction lines to their hydration unit, blender unit, or booster pump from this common manifold.

There are many advantages to treating water on site with this AOPP application. First, the entire volume of frac fluid is treated to kill bacteria, precipitate hardness salts thereby inhibiting scale deposition, oxidize heavy metals to also prevent scale, and oxidize soluble organics such as oil and grease. This solution is an alternative to liquid chemicals such as biocide and scale inhibitors. Therefore, the operator does not have to transport and store hazardous chemicals on site. Secondly it is cheaper to transport ground water, flowback and/or produced fluid to the next frac location as opposed to taking it to an off-site facility first. Third, the operator saves the cost of disposing of these waters, which they would otherwise have to do. Finally, the operator reduces the amount of fresh water required to complete their wells. On the 130 wells completed using the AOPP frac tanks since November 2009, the average reclamation percentage has been approximately 20%. The average frac volume is approximately 125,000 bbl. That is approximately 3,250,000 bbl of fresh water saved.

The disadvantage of the AOPP frac tank setup is the space it requires on location. To address this concern, a new AOPP design has been engineered to incorporate the technology in a smaller footprint. The AOPP system was redesigned to incorporate an 80 bbl per minute treatment capacity in a single 53-foot trailer. For fracs requiring more than 80 bbl per minute treatment capacity, two units would be deployed in tandem. These trailers (if using two in tandem) would be rigged up on location between the water source and the working frac tanks rigged up directly to the blender and pumping equipment. The 80 bbl per minute system will be fielded and tested in 3Q11.

Treatment Results - Bacteria Treatment

The AOPP frac tanks have been used on over 130 completed wells since November 2009, having treated over 16 million barrels of fluid on-the-fly on location during hydraulic fracturing operations. The influent over that period carried sulfate-reducing bacteria (desulfovibrio) (SRB) levels as high as 11,000,000 most probable number per milliliter, or 1×10^7 mpn/ml. The majority of influent samples over that period ranged between 1×10^3 and 1×10^6. To summarize the effectiveness of the treatment over that period, Table 1 shows the percentile of effluent samples that show SRB levels less than the given mpn/ml values.

Treatment Standard - Effluent Quality	Samples Meeting Given Standard	Total Sample Size	P - Value
$< 1 \times 10^1$ mpn/ml	229	291	79%
$< 1 \times 10^2$ mpn/ml	257	291	88%
$< 1 \times 10^3$ mpn/ml	285	291	95%

Table 1: Sulfate-Reducing Bacteria Treatment Results

We have focused this study on sulfate-reducing bacteria because they cause such significant documented problems downhole. SRB can survive at extreme temperatures, salinity, pH and pressure. SRB convert sulfate ions to hydrogen sulfide. Hydrogen sulfide can then form iron sulfide in the presence of steel. SRB proliferation may lead to corrosion, natural gas quality degradation, iron sulfide scale and safety issues associated with toxic hydrogen sulfide gas.

An independent third-party conducted studies to validate the AOPP frac tanks' ability to treat for bacteria on-the-fly during the hydraulic fracturing treatment of two specific wells. The temperature was approximately 85°F. The max pump rate for this particular frac job was approximately 100 barrels per minute. The independent third-party took the influent and effluent samples. Split samples were tested by two different laboratories using the most probable number method as outlined in Standard Methods, Section 9221C. The maximum reading of the bacteria enumeration technique was 140,000 mpn/ml, and several of the samples resulted in a reading of "greater than 140,000 mpn/ml". For the purposes of graphing the data, we used 140,000 mpn/ml for those data points; however, the actual bacteria level is greater. Figure 2 shows one set of samples from 22 stages across two wells on the same well pad. The results from these two wells are representative of the broader set of bacteria treatment results collected from the AOPP frac tanks since initial fielding in 2009.

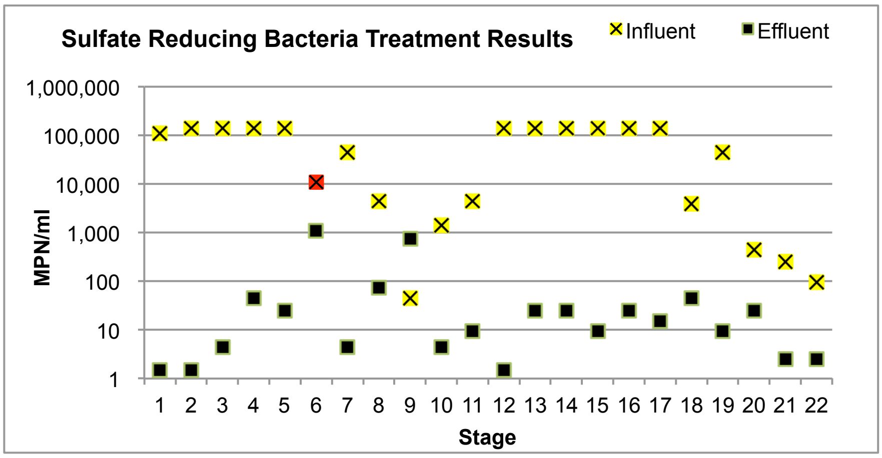

Figure 2: Sulfate-Reducing Bacteria Treatment Results

Treatment Results - Scale Inhibition

As stated previously, the passage of electricity through the water is the primary driver in precipitating hardness salts in the fluid. In addition, flash precipitation of hardness salts may occur locally near cavitation implosions. Finally, ozone gives assistance in the prevention of scale, oxidizing iron that can act as a building block in the crystallization of a scale matrix. Ultrasound breaks apart the precipitated salts into nano-sized suspended particles that will not cause scale.

The dynamic tube-blocking test is commonly used to test the efficacy of scale inhibitors on different waters. The test consists of pumping fluid through 1/16" pipe in a lab in pressure and temperature-controlled conditions. If the system pressure increases while pumping fluid through the system over time, then scale is forming in the pipe, decreasing the pipe cross-sectional area. When testing a liquid chemical scale inhibitor, the chemical is injected at the beginning of the system at varying ratios to determine the optimal concentration for a given type of water. The successful ratio is identified by the lack of pressure buildup in the system during the test.

Dozens of tube-blocking tests have been completed on water treated by the AOPP in the Woodford, Fayetteville, Eagle Ford and Haynesville shales. All tests have confirmed that the AOPP system inhibits scale deposition.

On a multi-well shale frac completed in September 2010, the AOPP treated fluid was sent to an independent laboratory to have tube-blocking tests conducted. Figure 3 shows that the flowback and fresh water mixture deposited scale during the tube-blocking test, as indicated by the increase in pressure during the test. The same fluid treated through the AOPP system showed zero scale deposition during the test.

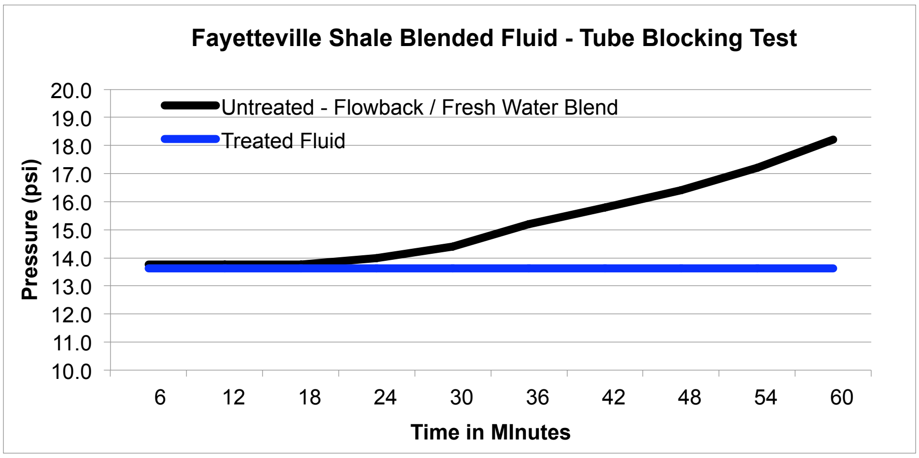

Figure 3: Dynamic Tube-Blocking Test Results, Fayetteville Shale Well

During a pilot study treating Eagle Ford shale flowback fluid, tests were conducted to compare the effectiveness of the AOPP system against other scale inhibition solutions. The independent laboratory tests show that fluid treated with the AOPP showed zero scale deposition in the tube-blocking test. Table 2 shows the pumping pressures during the test of untreated fluid, scale-inhibitor treated fluid and AOPP-treated fluid. The data show that AOPP-treated fluid pumps at lower pressures than fluid treated with standard scale inhibitors. The table compares the pumping pressures of these different waters to a baseline fluid, which in this case is deionized water (DI). Deionized water has had organics and ions removed via filter, membrane and/or ion exchange. AOPP-treated fluid pumps at 6% greater pressure than DI fluid, whereas scale inhibitor treated fluid pumps at 18% greater pressure than DI fluid.

	Untreated Fluid	Scale Inhibitor Treated Fluid	AOPP Treated Fluid
% Increase from DI	83%	18%	6%
Pressure Increase from DI (psig)	9.1	2.0	0.6

Table 2: Percentage Differences in Pumping Pressures of Different Fluids During Tube-Blocking Test

This data, along with corroborating anecdotal field evidence, suggests that, perhaps due to water density differences, fluid treated by the AOPP may require less hydraulic horsepower on fracs to achieve the same reservoir stimulation quality than fluid treated by liquid scale inhibitor. More data is required to scientifically substantiate this hypothesis, but initial data and anecdotal evidence are promising. This is a different "slicking" effect than the one addressed in the next section that covers friction reducer compatibility. Figure 4 shows the results of the dynamic tube-blocking test from the Eagle Ford shale pilot.

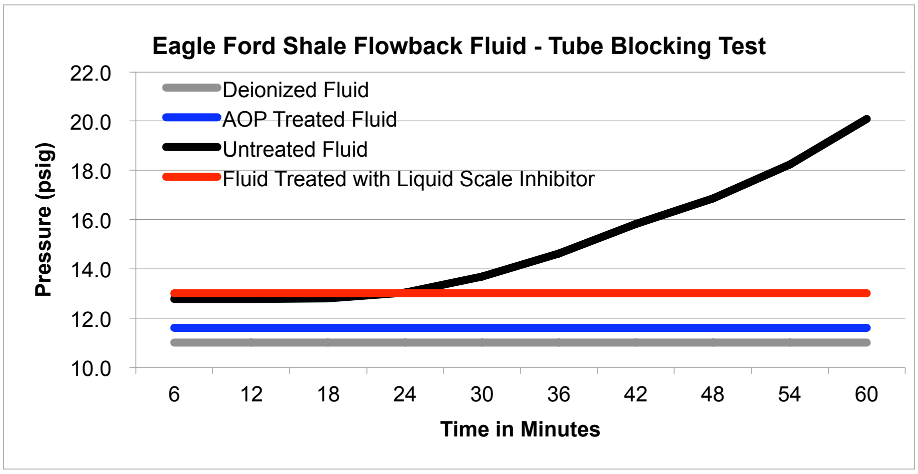

Figure 4: Dynamic Tube-Blocking Test Results, Eagle Ford Shale Flowback Fluid

Figure 5 shows the results of the dynamic tube blocking test on untreated and treated produced fluid from the Woodford shale. This fluid contained approximately 170,000 mg/l of dissolved solids.

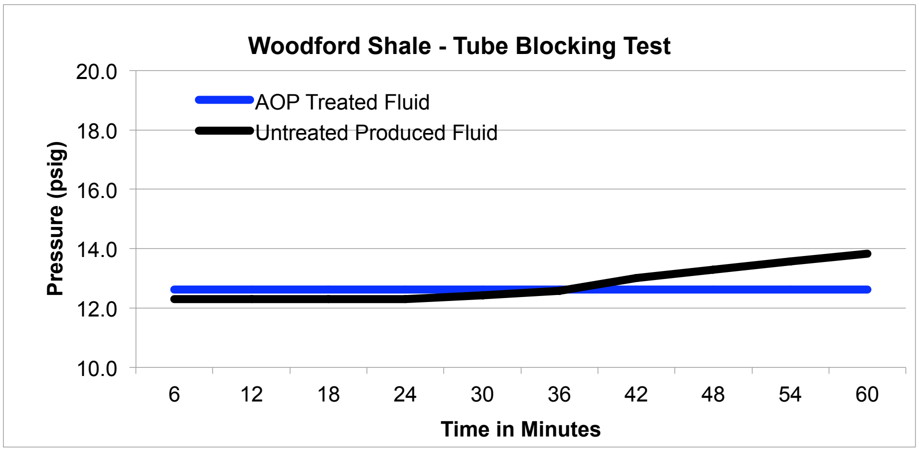

Figure 5: Dynamic Tube-Blocking Test Results, Woodford Shale Produced Fluid

Friction Reducer Compatibility

Flowback and produced fluid have higher levels of multivalent cations such as iron, calcium, barium and strontium. These cations interfere with the industry-preferred friction reducer (FR) used on most slickwater fracs, which is generally a negatively charged polyacrylamide friction reducer. One challenge the industry faces concerning recycling of high-salinity fluids is the compatibility of those fluids with FR. Cationic and nonionic friction reducers are being developed to respond to this challenge, but these FRs are generally 50% to 200% more expensive than the standard anionic version. In addition, the cationic and nonionic FRs do not mix as well in water. Based on observation of treating pressures we have noted a reduction in concentration of friction reducer used on AOPP frac jobs, but we have yet to collect adequate data to quantify the effect.

The same electrochemical reactions taking place in the AOPP would theoretically cause AOPP-treated high-salinity fluids to interact with anionic FR more efficiently. Since the AOPP precipitates these cations with anionic counterparts, the cations are no longer electrically active in the fluid to interfere with the anionic FR. Anecdotal feedback from the field as well as the water treatment chemistry support the hypothesis that AOPP-treated high salinity fluid would be more compatible with high salinity fluid than the same fluid would otherwise be with anionic FR. However, this hypothesis has yet to be confirmed with relevant data as have the bacteria and scale treatment aspects of the technology.

Economic Viability and Environmental Impact Case Study - Marcellus Shale

In order to show the economic and environmental impacts of the onsite, on-the-fly AOPP system addressed in this paper, a model was created to capture the costs associated with water management for hydraulic fracturing operations. Some costs addressed are the price to buy water, the price to transport it, the price to rent frac tanks, the price to treat it with chemicals during the frac, the price to dispose of fluid, and so forth. This scenario models one fictitious operator drilling and completing approximately 100 wells per year in Western Pennsylvania in the Marcellus shale, averaging 2 wells per pad. The nearest acceptable saltwater disposal is an underground injection facility in Eastern Ohio. One key assumption for the savings attributed to using the onsite AOPP system is that recycling flowback and produced fluid on subsequent fracs requires less trucking (via 120-barrel wheeled transport) than disposing of the same fluid at the saltwater injection well in Ohio.

In order to show the appropriate outputs, \$1.25/bbl was used as the cost for the treatment of water by the AOPP systems on location on-the-fly. This cost would vary based on monthly volumes treated by the systems as well as fluid characteristics. Tables 3, 4, 5 and 6 show assumptions used in the model concerning completion planning, disposal, water storage and water truck transportation:

Well and Customer Data	
Geological Formation	Marcellus
Geographical Area	Western PA
Wells Planned per Year	100 wells
Pressure Pumping Crews Utilized	2.0 crews
Average Number of Wells per Pad	2.0 wells
Max Treatment Rate	120 bpm
Average Treatment Rate	60 bpm
Stages per Well	14 stages
Barrels per Well	140,000 bbl

Table 3: Model Assumptions - Well and Customer Data

Truck Transportation	
Vehicle Fuel Burn Rate	5.00 gal/hr
CO_2 Emissions per Gal Diesel Burned	22 lbs CO_2 / gal
Water Truck Capacity	120 bbl
Truck Speed, Primary Roads	50 mph
Truck Speed, Secondary Roads	25 mph
Road Repair Cost Per Mile Driven	$ 0.25 / mile

Table 4: Model Assumptions - Truck Transportation

Water Storage	
Additional Tanks Required to Store Recycled Fluid on Location	8 tanks
Frac Tank Capacity	435 bbl
Frac Tank Rental Rate	$ 45 /day
Days Frac Tanks on Location	12 days

Table 5: Model Assumptions - Water Storage

Disposal	
Disposal Site	Eastern Ohio
Round Trip to Disposal	300 mi
Trucking Transport Cost per Hour	$ 95 /hour
Equivalent Cost per Barrel	$ 5.07 /bbl
Disposal / Injection Cost	$ 1.00 /bbl

Table 6: Model Assumptions - Truck Transportation

The model assumes both biocide and scale inhibitor are fully replaced by the process. We assumed a 10% increase in effectiveness of the anionic friction reducer using AOPP-treated fluid versus non-AOPP-treated fluid. Table 7 shows the cost of chemicals replaced or reduced by using the AOPP system. Table 8 includes the assumptions concerning the frac fluid composition the operator might currently be employing. Table 9 shows the frac fluid composition an operator might employ when using the onsite, on-the-fly AOPP system.

Chemicals Normally Used When Not Employing AOPP System			
Purpose	Concentration	Cost per Gal of Chemical	Resulting Cost per Barrel of Frac Fluid
Biocide - Glut/Quat	0.45 gal/mgal	$ 20 /gal	$ 0.38 /bbl
Scale Inhibitor - Phosphonate	0.35 gal/mgal	$ 20 /gal	$ 0.29 /bbl
Friction Reducer - Anionic	0.50 gal/mgal	$ 40 /gal	$ 0.63 /bbl

Table 7: Model Assumptions - Chemicals Used When Not Employing AOPP System

Frac Fluid Composition When Not Using AOPP System			
	TDS of Fluid	Percentage of makeup	Equivalent volume
Surface Water	500 mg/l	90%	126,000 bbl
Flowback Fluid	30,000 mg/l	10%	14,000 bbl
Produced Fluid	230,000 mg/l	0%	0 bbl
	Resulting TDS of Blended Fluid	3,450 mg/l	

Table 8: Model Assumptions - Frac Fluid Composition When Not Using AOPP System

Frac Fluid Composition When Using AOPP System			
	TDS of Fluid	Percentage of makeup	Equivalent volume
Surface Water	500 mg/l	50%	70,000 bbl
Flowback Fluid	30,000 mg/l	30%	42,000 bbl
Produced Fluid	230,000 mg/l	20%	28,000 bbl
	Resulting TDS of Blended Fluid	55,250 mg/l	

Table 9: Model Assumptions - Frac Fluid Composition When Using AOPP System

Table 10 addresses two sets of assumptions used in the model. The first set of assumptions is the transportation cost for moving the fluid to be used for the frac to location. This model assumes that the surface water used for the frac is pumped onto location from a nearby source, and that the variable cost to pump this water is approximately $0.10/bbl. The model assumes that the flowback and produced fluid will have to be trucked onto location to be stored in a frac tank and that trucking cost is approximately $1.21/bbl. The second set of assumptions concern the cost to purchase water. In many cases, the operator must purchase water from lakes, rivers, streams or municipalities. This cost is offset for every barrel of wastewater recycled. The flowback and produced fluid are traditionally a waste product and no purchase cost is assigned.

Cost To Transport and Purchase Fluid for Frac		
	Cost to Transport Fluid from Source to Location	Cost to Purchase Water
Surface Water	$ 0.10 /bbl	$ 0.50 /bbl
Flowback Fluid	$ 1.21 /bbl	$ 0.00 /bbl
Produced Fluid	$ 1.21 /bbl	$ 0.00 /bbl

Table 10: Model Assumptions - Cost To Transport and Purchase Fluid for Frac

Table 11 shows the net economic benefit of using the AOPP system in this scenario. For example, if it costs $5.07 to transport fluid to a disposal facility and $1.21 to transport the same fluid to a well to be used for frac fluid, the net savings to the customer for trucking is $3.86 per barrel for every barrel of fluid recycled. The scenario assumes two independently operating sets of AOPP systems cover all completions for the operator, with each set of AOPP systems moving with a respective frac crew.

Economic Impact		
	Impact per Well	Annualized Impact
Water Management	**$ 325,749**	**$ 32,574,917**
Road Damage from Trucking	$ 29,167	$ 2,916,667
Trucking and Disposal	$ 271,973	$ 27,197,333
Purchase and Pump Fluid	$ 33,600	$ 3,360,000
Storage	$ (8,991)	$ (899,083)
Chemicals	**$ 102,900**	**$ 10,290,000**
Biocide	$ 52,920	$ 5,292,000
Scale Inhibitor	$ 41,160	$ 4,116,000
Friction Reducer	$ 8,820	$ 882,000
Gross Operational Savings	**$ 428,649**	**$ 42,864,917**
AOPP Treatment Price*	**$ (175,000)**	**$ (17,500,000)**
Net Savings to Customer	**$ 253,649**	**$ 25,364,917**

**Dependent on monthly volume treated and water characteristics.*

Table 11: Economic Impact of Using AOPP Systems On-The-Fly During the Frac

Table 12 shows the resulting environmental impact of using the AOPP systems in this scenario. For every barrel of fluid recycled, one barrel of fresh water is conserved. The model also captures the amount of liquid chemicals eliminated entirely from the fracturing operation. A reduction in truck traffic contributes to fewer greenhouse emissions. The same variable obviously contributes to trucking miles eliminated, which would have a positive impact on the surrounding community. The reduction in trucking man-hours would lead to a safer overall operation and safer roads in the operating area.

Environmental Impact		
	Impact per Well	Annualized Impact
Fresh Water Saved	2,352,000 gal	235,200,000 gal
Liquid Chemicals Eliminated	4,925 gal	492,450 gal
Greenhouse Emissions Reduced	6,475 Tons CO2	647,500 Tons CO2
Miles of Trucking Eliminated	116,667 miles	11,666,667 miles
Trucking Man-Hours Eliminated	2,333 man-hours	233,333 man-hours

Table 12: Environmental Impact of Using AOPP Systems On-The-Fly During the Frac

Summary and Ongoing Work

The AOPP can replace liquid biocides and scale inhibitors while at the same time allowing operators to recycle 100% of their flowback and produced fluid. This on-the-fly, high-rate treatment system can be used on location as a pretreatment for frac fluid just before it goes downhole, thereby eliminating a logistical node created by an offsite facility. The challenge for the operator is then lessened to providing the necessary planning and storage for the water it will reuse. The AOPP does not require specific tailoring to water quality having been successful on waters ranging from surface water to groundwater to high-salinity produced fluid. There is no waste stream created by the process and this philosophy of treating the fluid without a by-product and pumping it all downhole has been confirmed by the millions of barrels of fluid that have already been pumped into successful, economic producing wells. As the water treatment requirements for fracturing expand while our sources of fluid become more strained, a powerful, economic, onsite treatment such as the AOPP will play a critical role in the development of the vast resources locked in tight reservoirs beneath American soil.

Conclusions

- A mobile advanced oxidation and precipitation water treatment system that can provide microbial and scale control to operators during hydraulic fracturing operations has been successfully field-tested and proven cost effective over the past two years.
- The system is designed to work independently with internal generators.
- The only moving parts in the system are pumps and generator power systems. This allows for tremendous ease in maintenance and reliability.
- The AOPP solves problems concerning chemical compatibility and also offsets some of the industry's consumptive use of fresh water by allowing operators to recycle its wastewaters.
- The process is economical due to the chemicals it replaces during the fracturing process, as well as the trucking and disposal prices mitigated by recycling flowback and produced fluid.
- Ongoing customer-feedback-inspired engineering alterations to the equipment have lessened the footprint from 10 to 12 frac tanks down to the equivalent footprint of two frac tanks.
- The newest design can economically treat fresh water or fresh water / brine mixtures at 80 barrels per minute.
- Another distinct advantage of the process compared to competitive systems is there is no waste stream. All materials become non-reactive and are pumped downhole, eliminating the need to extract waste from the water volume.
- GREEN: By eliminating chemicals in the treatment there is less concern for contamination of aquifers and possible danger to personnel handling chemicals on site. Eliminating truck traffic by recycling fluid has numerous environmental benefits.

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