"Minimum Effective Dose: A Study of Flowback and Produced Fluid Treatment for Use as Hydraulic Fracturing Fluid"
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Abstract
This paper outlines results from 15 months of flowback and produced fluid treatment for use as hydraulic fracturing fluid in the Permian Basin in Texas and in New Mexico in the Delaware basin. It has been used on 177 wells and 3,075 stages in this area during the period, having been used to treat 21.7 million barrels of fluid: 4.5 million barrels of which was reused flowback and/or produced fluid. The technology employs the minimum effective treatment for water reuse for frac, addressing microbial control, scale inhibition, and frac chemical compatibility. Tube-blocking tests are used to demonstrate scale inhibition, standard serial dilution bacteria analyses demonstrate bacteria treatment, and both laboratory friction loop tests and actual friction reducer usage statistics demonstrate frac fluid compatibility. This paper will summarize the operating history of the technology and will address results from various analyses conducted on water treated by this advanced oxidation and precipitation water treatment process that provides on-the-fly treatment at approximately 80 barrels per minute.

Introduction
As hydraulic fracturing continues to fuel steady drilling activity across the United States, the need for the industry to reuse its wastewater—flowback and produced fluid—continues to become more important. A large percentage of the activity in the US happens to be in areas with water scarcity, like Texas, northern Oklahoma, and North Dakota. There are two challenges when reusing wastewater for frac: logistics and water quality.

The advanced oxidation and precipitation process (AOPP) is used as an on-the-fly water treatment process for hydraulic fracturing operations. The equipment has the footprint of two frac tanks and generally occupies space behind the working tanks on a frac location. The equipment is designed to be a pass-through process on a frac site, providing a simplification of the logistics of recycling water. The AOPP is designed to accept particularly challenging fluid at very high rates—approximately 80 barrels per minute (bpm)—and provide bacteria treatment, scale inhibition, and frac chemical compatibility improvement. In order to provide a minimum effective treatment for any fluid for fracturing, these three issues must be addressed. The technology allows operators to reuse large quantities of flowback and produced fluid ("reused fluid") while eliminating the need for any additional treatment on location or at an offsite location. The technology replaces standard biocides and scale inhibitors typically used on location to treat frac fluid while improving friction reducer compatibility with extremely complex water matrices.

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 design consists of an AOPP unit that processes fluid at 80 bpm. A generator contained separately provides electrical power. Water enters the system through two 10” pipes traveling through 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 and organic compounds. In a controlled environment ozone is an extremely safe oxidant with which to work. The 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 hydroxyl radicals and causing thermochemical decomposition. 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 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 uses no liquid chemicals and creates negligible waste. Instead of providing separation of divalent ions like calcium, barium, sulfate and carbonate, the AOPP precipitates these dissolved solids into

* Typical waste generated by the process is approximately 20 lbs of solids per 100,000 bbl treated, or 0.0005% by mass.
colloidal solids and all of the matter is pumped downhole (Ely et al. 2011).

Operational Experience from November 2011 to February 2013
The AOPP equipment has been used predominantly in Texas in the Permian basin in the Wolfcamp play southeast of Midland, and also in southeast New Mexico in the Delaware basin with a company targeting a series of geologic horizons. From November 2011 to February 2013, the technology has been used on 177 wells, the large majority of which were slickwater fracs, or fracs involving the use of friction reducer instead of a gelling agent. The size of the fracs for single wells ranged from 10,000 bbl to 416,000 bbl; from 1 to 46 stages. The total volume treated over this time period was 21.7 million bbl on 3,075 stages. The equipment uptime for the period has been 99%.†

Since the AOPP equipment is designed to treat all water that goes downhole on a frac, the average blend of fluid treated by the process is an 80:20 blend of fresh water to reused water. The AOPP process has allowed an operator in the Permian Basin to increase its ratio of reused water significantly, as shown in Fig. 1. In November 2011, the operator did not reuse its wastewater in this region. In 1Q13, the same operator’s average frac fluid comprises 28% reused fluid from other wells in its field. Fig. 2 depicts the volume of water treated by the AOPP equipment over 15 months, and highlights the significance of the operator’s reuse program.

Treatment Results - Bacteria Treatment
For the bacteria treatment study, samples of water from before and after treatment by the AOPP equipment were taken across 10 wells from May to July 2012 in west Texas, with temperatures in the region during that time of year providing the most challenging circumstances for bacteria treatment of frac fluids. Approximately 4 samples were taken from each well during standard fracturing operations while the AOPP equipment was treating fluid at approximately 80 bpm. An independent third-party laboratory in Midland, TX, conducted the bacteria analyses. It used standard serial dilution methods to quantify general heterotrophic, sulfate-reducing, and acid-producing bacteria.‡ The samples were delivered to the lab within twenty-four hours and were kept in a cooled environment during transit. The lab returned bacteria results in most probable number per milliliter (MPN/mL).

Fig. 3 shows the results from the study chronologically, starting with the first sample from the first well in May, ending with the last sample in July. The makeup of the fluid treated included as high as 43% reused fluid. The results depicted in Table 1 show the combined total of all bacteria tested, both for untreated and treated samples. Results show higher than 99.29% reductions of bacteria in every month, and an average of 99.70% bacteria reduction throughout the time period.

Treatment Results - Scale Inhibition
The tube-blocking test was used to test the AOPP equipment’s ability to reduce scaling tendency. The tube-blocking test is a commonly used method for testing the efficacy and dosage requirements for commercial oilfield liquid scale inhibitors. The test involves pumping fluid through a 1/16” stainless steel tube over the course of several hours. Samples are pre-filtered for suspended solids to prevent plugging in the apparatus. Therefore, the only factor that would cause a system pressure increase over time would be mineral scale deposition in the pipe, effectively decreasing the internal diameter of the tube. Since the flow rate is kept constant, an increasing pressure profile over time indicates that given water is depositing scale in the pipe. The pipe is routed through an oven to raise the temperature of the fluid, thereby encouraging the deposition of the most common form of scale: calcium carbonate. If there is no pressure increase over time, then the water is considered to have no scaling tendency. A successful scale inhibitor test will reduce the total net pressure buildup by 67%. In other words, if after 8 hours of test time on untreated water yields a differential pressure of 10 psig (all tests start at 0 psig), then the same water treated with an effective dose of scale inhibitor would yield a differential pressure of less than 3.3 psig over an 8 hour period.

Dozens of tube-blocking tests have been conducted on waters treated by the AOPP equipment in various locations. The tested water has varied in total dissolved solids (TDS) from 1,500 milligrams per liter (mg/L) TDS to

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1 Calculated by taking total number of stages upon which the equipment provided effective treatment (3,075), divided by the total number of stages upon which the equipment was assigned to treat water (3,102).

2 Some results were given in ranges. For these results, the mid-point of the range was used for calculation and graphing purposes.
180,000 mg/L TDS. The AOPP equipment consistently inhibits scale, as normally indicated by the tube-blocking test results.

Fig. 4 shows the results from a tube-blocking test conducted on 39,000 mg/L TDS fluid treated at 80 bpm in the Permian Basin. This is a typical result from this test on water treated by the AOPP equipment. The untreated water deposited mineral scale in the tube during the test, resulting in an ending pressure differential of 9.3 psig after 13 hours of run time. The treated water resulted in an ending pressure differential of 0.4 psig after 13 hours of run time, or a 96% effective reduction in pumping pressure.

**Friction Reducer Compatibility**

Flowback and produced fluid have higher levels of multivalent cations such as calcium, barium, and iron. These cations can interfere with the most common type of friction reducers used in slickwater fracs: the anionic polyacrylamide friction reducer (FR). This effect on FR can cause multiple problems on a frac, to include increased pumping pressures and FR usage, both of which result in increased cost.

The AOPP equipment improves compatibility of anionic FR with high-TDS fluid through the same mechanisms that allow the equipment to inhibit scale. The multivalent ions are precipitated into suspended solids that are much less reactive; rendering a fluid that is more compatible with negatively charged chemicals such as FR. Two separate studies, one in a laboratory, and one study of actual FR usage in the field, indicate that the AOPP equipment effectively improves FR compatibility with high-TDS fluids.

**Friction Loop Test.** Water treated at 80 bpm by the AOPP equipment in west Texas was sent to a laboratory in Duncan, OK, to be tested for FR compatibility using a standard friction loop test. The friction loop test simulates flow conditions on a frac in order to quantify the friction reduction rendered by common drag-reducing agents such as FR. The lab first injected 0.5 gallons per thousand gallons (gpt) of anionic FR while pumping Duncan tap water. It then ran the same procedure with untreated flowback fluid, which had 81,500 mg/L of TDS. Finally, the lab ran flowback that had been treated with the AOPP equipment. The results indicated a 27% improvement in friction reduction over a 30-minute time period. **Table 2 and Fig. 5** show the results.

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<th>TABLE 2—FRICITION LOOP TEST RESULTS, UNTREATED VERSUS AOPP TREATED FLUID</th>
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**FracFocus Study of Friction Reducer Usage.** FracFocus§ is a chemical disclosure registry that allows operators to voluntarily disclose the chemical makeup of frac fluid used in hydraulic fracturing operations. The data include friction reducer usage for multiple wells in the area where the AOPP equipment is being used to treat water for fracs. A study of the FR usage (reported as percentage mass by FracFocus) indicates that FR usage by an operator employing the AOPP equipment yielded a reduction in FR usage during a period of increased water reuse.

On 10 wells hydraulically fractured from February to August 2011 where the AOPP equipment was not used to treat the frac fluid, the average FR usage as a percentage mass was 1.66%. The water makeup for the fracs consisted of nearly 100% fresh water. Comparatively, on 22 wells fractured during a six-month period from February to July 2012, the average composition of the frac fluid included 16% reused water (flowback and produced fluid). An expected outcome would be an increase in FR usage, given that the FR product remained predominantly the same and the water quality decreased. Instead, the average FR usage during the period was 1.45%, representing a 12.7% reduction in FR usage.” Given the friction loop test results mentioned previously, it is reasonable to attribute this FR usage reduction to the AOPP technology. **Fig. 6** shows a graph of the data.

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§ www.fracfocus.org/chemical-use

**Wells that reported zero FR usage were omitted, since these are most likely reporting errors, though this didn’t significantly impact the results. Also, the operator changed FR types in July 2012, so that data was omitted as well.**
Summary
The AOPP equipment can replace liquid biocides and scale inhibitors for hydraulic fracturing operations, while allowing operators to safely reuse large quantities of flowback and produced fluid as frac fluid. The technology is field-proven, having been used on hundreds of wells, only a portion of which has been the focus of this paper. The technology accomplishes this in a small footprint without the use of liquid chemicals or the generation of waste. The process has been tested in field operations during live fracs for its capacity to control bacteria, inhibit scale, and improve friction reducer compatibility. These tests indicate that the AOPP equipment provides the minimum effective treatment required to safely reuse wastewater for fracturing operations.

Conclusions
• A mobile advanced oxidation and precipitation water treatment system effectively treats flowback and produced fluid so it can be reused as frac fluid.
• The system requires a footprint of approximately two frac tanks, treats at 80 bpm, uses no liquid chemicals, and generates negligible waste.
• The focus period for this study included a 15-month period during which the AOPP equipment was used to treat nearly 20 million barrels of fluid on nearly 3,000 stages with 95% uptime.
• The AOPP equipment has allowed an operator in the Permian Basin to increase the reused fluid makeup of its frac fluids from zero to 28% in a 15-month period, resulting in 4 million barrels of water reused.
• Treatment results indicate effective microbial control in the challenging environment of a west Texas summer.
• Treatment results indicate effective scale inhibition for 39,000 mg/L TDS fluid treated at 80 bpm, although a large body of test results indicate that there is effectively no TDS limit on the scale inhibition treatment capabilities of the equipment.
• Friction loop studies and analysis of FracFocus data indicate that the AOPP equipment is allowing an operator to decrease its friction reducer usage while increasing its wastewater reuse rate.

References

Author Bios
Aaron Horn is Sr. Technical Advisor to Hydrozonix, where he previously served as President. Aaron also served as President of Ecosphere Energy Services, the company that holds the license to the AOPP technology addressed in this paper. Prior to that Aaron served as an Operations Engineer for Newfield Exploration in Tulsa, OK. Aaron is a combat veteran and holds a BS degree in systems engineering from the United States Military Academy at West Point, NY.

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APPENDIX—FIGURES

Figure 1—Flowback and produced fluid reuse rate shown as a percentage of total frac fluid volume for a Permian Basin operator using AOPP equipment.

Figure 2—Depiction of fluid treated by AOPP equipment and the percentage that was reused water.
**Figure 3**—Bacteria treatment results from AOPP water treatment from 38 samples across 10 separate wells in the Permian basin from May to July 2012. Results show the combined total of general heterotrophic, sulfate-reducing, and acid-producing bacteria. The scale of the chart was set from 0 to 100,000 MPN/mL in order to depict the data clearly. However, two values (610,500 and 1,650,000) go beyond the scale of the chart and are depicted here with labels.

![Graph showing bacteria treatment results](image)

**Figure 4**—Tube-blocking test result from water treated for frac in Permian basin. Treated water showed 96% reduction. Water contained approximately 39,000 mg/L of TDS and was treated at 80 bpm.

![Graph showing tube-blocking test results](image)
Figure 5—Friction loop test results for untreated and AOPP treated, 81,500 mg/L TDS fluid. 0.5 gallons per thousand **gallons** of anionic friction reducer dosed for each fluid type.

Figure 6—Results from study of FracFocus data on friction reducer usage for 32 wells. 10 wells were studied in a six-month block of time prior to the operator using the AOPP equipment addressed in this paper. Then 22 wells were studied from a six-month block of time after the operator started using the AOPP equipment. The figure also shows the flowback reuse rate.