AN OVERVIEW OF THE WATER TREATMENT MARKET AND TECHNOLOGY
WITH A FOCUS ON THE PERMIAN BASIN

by

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Summary

The near and long term trends in the water treatment industry are positive. Water treatment and recycling have environmental and cost savings benefits; therefore efforts are underway to treat a greater percentage of produced water and to build out the pipeline, storage and treatment infrastructure to continue improving the economics of water treatment and logistics.

The purpose of this article is to characterize and quantify frac water, flowback water and produced water, and discuss issues, costs, technologies and trends in water management with specific focus on the Permian Basin. This paper provides illustrative costs associated with the treatment of flowback and produced water and its reuse as frac water. Water purchase, transportation, storage, treatment and disposal costs vary widely depending on source locations, shipping distances, modes of transportation, and water quality. The reuse of flowback and produced water is economical if there is sufficient fracking activity near the source of produced water such that water storage and transportation costs are not prohibitive.

Industry Primer and Market Overview

The hydraulic fracturing of a hydrocarbon reservoir requires the consumption of water, sand and chemicals (“frac water,” “frac sand” or “proppants” and “frac chemicals”). Generally, 20% to 40% of frac water returns to the surface soon after the well completion process. The remainder of the fluid absorbs into the shale formation. Together with this returning water are portions of the frac chemicals, frac sand and a small quantity of oil from the reservoir. This mixture is known as “flowback water” or simply “flowback.” Through the life of a well, naturally occurring water is produced in association with oil and gas which is called “produced water” or “formation water”. Sources of frac water are untreated surface and groundwater water and treated waste water. More specifically, frac water includes untreated fresh and brackish water; treated flowback and produced water; treated municipal effluent; and blends of these sources.
Fresh water is a precious resource, and the disposal of flowback and produced water is expensive. The treatment and reuse of flowback and produced water conserves fresh water and reduces disposal costs. Furthermore, frac water treatment contributes to well integrity and hydrocarbon production rates and complements a production chemical maintenance program over the life of the well. Therefore, the best practice is to ensure that clean water without detrimental contaminants is used for hydraulic fracturing by treating frac water as it is being pumped onto the well site and introduced into the wellbore (called “on-the-fly” water treatment) regardless of whether it has been previously cleaned at a water storage location.

During the downturn since the fall of 2014, fracking slowed to the point that demand for frac water was low. In addition, the drought gripping Texas and the Southwest during the peak of the drilling boom has abated making fresh water more available. With fresh water and brackish water plentiful and less expensive, they have been the predominant water sources for fracs in the Midland Basin portion of the Permian, and the treatment of produced water has generally not been cost justified. With the price of oil now above $50/bbl following OPEC’s oil production cut announcement in late November 2016, fracking and well completions are increasing throughout the U.S., in particular, the Delaware Basin. The Delaware Basin is more arid than the Midland Basin and contains fewer and more distant disposal wells. Consequently, the activity in the Delaware Basin is increasing demand for fresh and brackish water alternatives and will improve the attractiveness of the treatment of flowback and produced water.

**Size of the Water Treatment Market**

According to the EPA, the U.S. annually consumes on the order of 1.7 to 3.3 billion barrels of water in fracking operations. This is equivalent to 70 to 140 billion gallons or 215,000 to
430,000 acre-feet annually.¹ The amount of water used in hydraulic fracturing may appear substantial, but it comprises approximately 0.1% of the total water used in the United States.² By comparison, the amount of water consumed in the irrigation of golf courses across the U.S. is 5.5 to 11 times the quantity of frac water usage.³ Furthermore, the oil and gas industry can satisfy much of its demand for frac water with the treatment and reuse of flowback and produced water rather than the consumption of fresh water which can largely offset the stress that frac water demand places on fresh water in some specific locations.

Produced water, however, is another matter. Its production in 2012 was estimated to be 21.2 billion bbl,⁴ 6 to 13 times that of frac water. In other words, the oil and gas industry can treat and reuse approximately 8% to 16% of produced and flowback water in subsequent fracking operations and a small additional quantity in enhanced oil recovery operations. The vast majority of produced water must be injected into disposal wells in today’s environment.

The size of the U.S. oil and gas water treatment market may be as high as $500 million per year.⁵ It shrunk during the downturn but may have exceeded this amount at its peak in 2013 and 2014. This market estimate excludes the biocide market typically served by production

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² Total U.S. water consumption is reported by the U.S. Geological Service to have been 355 billion gallons/d in 2010 in its every-five-year survey of water usage. See “Estimated Use of Water in the United States in 2010”, Circular 1405, U.S. Geological Survey (2014).


⁵ Authors’ estimate. This number is not readily available from public sources.
chemical companies during well completion and through the well life. When water sourcing, transportation, storage, filtration and disposal are considered, oilfield water management in total is a multi-billion dollar per year market. Increasingly, the large oil and gas producers and some oilfield service companies are building buried water pipeline systems to transport the vast quantities of fresh and produced water from water sources to central locations near well sites, treatment facilities and salt water disposal wells (“SWDs”).

The Permian Basin has more producing wells and drilling activity than anywhere else in the U.S. Though the Permian was discovered and developed decades ago, it remains the most prolific oil basin and a significant gas basin because of its large surface area and the number and thicknesses of its hydrocarbon-bearing strata. Furthermore, the Permian is the lowest cost region in which to produce oil owing to the favorable geology and a highly developed infrastructure of service companies, pipelines and processing plants. This explains why more rigs were operated in the Permian than elsewhere during the downturn, why the Permian was the first to recover after the rig count bottomed in May of 2016, and why approximately 40% of all drilling rigs in the U.S. today are operating in the Permian compared to 25% historically.6

Daily oil & gas production in the Permian relative to the U.S. as a whole is approximately 2.1 million bopd vs 8.8 million bopd (24% of the total) and 7.4 Bcf/d of gas vs 87.6 Bcf/d (8% of the total) for the U.S.7 The ratio of produced water to oil in the Permian (the “water cut”) is typically 5.0 or higher, depending on the field location. The water cut in the Permian generally exceeds that of the Eagle Ford or the Bakken. The amount of water production increases over time as hydrocarbon production declines.

6 Baker Hughes rig count data.
**Water Characteristics**

Both fresh and produced water contain bacteria, organic matter, minerals and metals. Unlike fresh water, produced water has a high content of total dissolved solids (TDS), most notably sodium chloride and other salts. The salinity of produced water in the Permian is approximately 100,000 ppm (or mg/L) compared to sea water at around 35,000 ppm. Salt tolerant crops (certain varieties of canola, rye, barley, wheat, cotton, and other plants) can handle salinity in the 4,000 to 10,000 ppm range; livestock can tolerate salinity up to 2,500 ppm; and humans can tolerate salinity up to 500 ppm.\(^8\)\(^9\) Therefore, careful control of salts and salt compositions is critical to water reuse, with specific limits dictated by end-use applications (i.e., oilfield vs. irrigation vs. potable water). Salinity control is quite challenging because treatment options are limited and costly and because significant residual by-products are produced. Virtually all processes employed for salinity reduction result in a concentrated liquid waste (brine) which must be disposed subsequently.

While bacteria, suspended organic matter, minerals and certain dissolved metals can be economically removed from water using common chemical and mechanical water treatment methods, most dissolved solids, such as chloride salts, cannot. Although containing high salinity (TDS), treated water can be used in hydraulic fracturing with proper selection of crosslinking agents in the frac chemical formulation, however, high TDS precludes discharge of treated water into a river or lake or use in municipal, agricultural, and industrial applications. The additional cost to remove salts via reverse osmosis, evaporation or other process can potentially be justified by the higher price commanded by potable water if a large enough population were to reside within reasonable proximity to the fields generating produced water. However, most production tends to be in less populated areas. As a result, a large quantity of

\(^8\) Benko and Drewes, Environmental Engineering Sciences, 25, 2, 239.

\(^9\) “Annex 1: Crop Salt Tolerance Data,” by the Food and Agriculture Organization of the United Nations.
produced water must end up in salt water disposal wells. SWDs are the most economical alternative to dealing with large quantities of such water.

Physical and chemical properties of produced water vary depending on many factors, such as reservoir geology, hydrocarbon composition, geographical location, and water injection history. The chemical composition of produced water will change during the production lifetime of a reservoir. Most production wells produce dry oil at the beginning of the field life. The water cut increases at an accelerated rate once the water/oil interface reaches the wells, this being known as “water breakthrough.” As oilfields age, water becomes the predominant fluid produced.

Flowback water, as the name implies, is water that flows back to the surface following the completion of hydraulic fracturing. The fluid contains clays, chemical additives, dissolved metal ions, and suspended solids. The water has a murky appearance from high levels of suspended particles. In contrast, produced water is naturally occurring water found in shale formations that flows to the surface throughout the entire lifespan of the well. This water over time has leached out TDS and minerals from the shale including barium, calcium, iron and magnesium. It also contains dissolved hydrocarbons such as methane, ethane and propane along with naturally occurring radioactive materials (NORM) such as radium isotopes\(^\text{10}\).

**Water Treatment Processes and Comparison of Biocides**

In the oilfield, a variety of water treatment methods are used or have been tried, including chemical water treatment processes; mechanical processes using equipment such as aerators, filters, centrifuges, hydrocyclones, gun barrels, weir tanks and clarifiers; ultraviolet light;

electrocoagulation; evaporation; and reverse osmosis. More than one method is often employed. Chemical and mechanical treatment is generally required in the treatment of produced water. Ultraviolet light, electrocoagulation, evaporation and reverse osmosis have limited applicability in the oilfield for cost or other reasons.

The biocides used in water treatment generally fall into two broad categories, oxidizing and non-oxidizing biocides.\(^\text{11}\) Oxidizing biocides include chlorine dioxide (ClO\(_2\)), peracetic acid (PAA), sodium hypochlorite (bleach), sodium chlorite, sodium bromide (hypobromous acid precursor), hydrogen peroxide, ozone, and potassium permanganate. Non-oxidizing biocides include organic aldehydes (formaldehyde, glutaraldehyde); quaternary ammonium compounds ("QACs" or "Quats", including methyl, benzyl, C-10, C-14, C-18 mixtures); organophosphorous (THPS, TTPC); organobromine (DBNPA); and organosulfur (isothiazalones and dazomet).

Oxidizing biocides are generally less expensive than non-oxidizing biocides. Inorganic chlorine and bromine based products (bleach and sodium bromide) are less expensive than organic based chlorine and bromine products, and generally less expensive than peroxygen based materials. Oxidizing biocides work well to control a broad variety of microorganisms commonly found in oilfield applications. Oxidizing biocides are fast-acting, usually killing bacteria within seconds or minutes of contact. The most attractive attribute of oxidizing biocide is that they are not persistent in the environment as they degrade rapidly in water and, therefore, can be fully reacted or neutralized to eliminate environmental discharge issues. Oxidizing biocides can be measured in real time by monitoring residual levels of oxidant in the water after treatment. This ensures that all oxidizable contaminants in the water, including bacteria, iron and H\(_2\)S are oxidized to yield a “clean brine” fluid for fracking.

\(^\text{11}\) Numerous references cover the topic of oxidizing and non-oxidizing biocides for which the authors are grateful. See, for example, “Directory of Microbicidal for the Production of Materials. A Handbook,” Edited by Wilfried Paulus, The Netherlands: Springer, 2005.
A downside of oxidizing biocides in circumstances when only bacteria are to be targeted is that higher dosages could be required if the untreated water has a high oxidant demand from constituents other than bacteria (i.e., organic matter, ammonia, organic nitrogen, hydrocarbons, hydrogen sulfide and iron, manganese and other metals). In addition, oxidizing biocides could be incompatible with scale inhibitors, corrosion inhibitors, frac treatment chemicals, and other common additives.

Non-oxidizing biocides are usually more expensive than oxidizing biocides. Non-oxidizers are slow to kill bacteria, and may not kill a broad array of bacteria. Some types of bacteria can become tolerant to non-oxidizers over time. Non-oxidizers often work on a distinct metabolic pathway. They may crosslink polypeptide chains or change cell membrane permeability. Many non-oxidizers react chemically with S-S and S-H bonds of amino acids found in the microorganism. This feature is often a detriment in oilfield water containing H₂S. Non-oxidizers are deactivated by H₂S, a common contaminant in oilfield operations. Also, since non-oxidizing biocides are difficult to measure in real time, treatment performance cannot be verified or dosages adjusted corresponding to changes in water conditions.

**Biocides in Hydraulic Fracturing Fluids**

Biocides are critical components of hydraulic fracturing fluid compositions.¹² Bacterial control is necessary to prevent excessive biofilm formation downhole that may lead to clogging and consequently hindering oil and gas extraction. Biocides inhibit growth of sulfate-reducing bacteria (SRB), which anaerobically generate H₂S and sulfides during the organisms’ respiration process. Sulfide species created in the subsurface may pose a risk regarding safety and health when the fluid returns along with produced H₂S gas. Furthermore, SRB and acid-producing

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bacteria (APB) may induce corrosion of the production casing/tubing underground, potentially leading to casing failure and environmental contamination by petroleum products.

The major sources of bacterial contamination are (1) drilling mud, (2) water, (3) proppants, and (4) storage tanks. Prolonged storage of water in large lined/unlined earthen pits or above ground storage tanks can lead to a proliferation of microorganisms. Likewise, bacteria can thrive in stored produced water being held for use in future fracturing operations. The increased temperatures fracturing fluids are exposed to underground may also favor microbial growth, and therefore many bacterial species (including anaerobic species that are native to shale formations) may proliferate underground during hydraulic fracturing.

Many biocides are short-lived, degrading through physical and biological processes, but some, especially non-oxidizing biocides, may transform into more toxic or persistent compounds. Slowly degrading and chemically persistent biocides may be a source of environmental contamination during flowback operations. Knowledge of biocides’ behavior under downhole conditions (high pressure, temperature, and salt and organic matter concentrations) is limited.

**Chlorine Dioxide (ClO2) Use in Hydraulic Fracturing**

With the rapid development of hydraulic fracturing, chlorine dioxide has emerged as a leading microbiological control technology for frac water disinfection. It is a powerful biocide that has been used commercially in the oilfield for over 25 years to control microbiological activity, prevent souring by H$_2$S and improve flow assurance.$^{13}$ Chlorine dioxide is an optimal solution for on-the-fly treatment of frac water because it is highly effective on both bacteria and biofilms and requires lower dosages than other technologies. It is very effective at removing H$_2$S, sulfides, and iron from water which have harmful effects on well casing. Chlorine dioxide

allows real time monitoring and control and has a proven Safety, Health, and Environmental footprint (a “green biocide”). ClO₂ has the advantage over bleach and some other oxidizing biocides because it is effective as a biocide at all pH ranges and does influence the pH of the treated water.

In addition to an oxidizing biocide, a non-oxidizing biocide such as glutaraldehyde is often added to the frac water and proppant formulation to provide biocontrol within the wellbore and nearby reservoir. Since downhole conditions impact the performance of biocides, it is not known how effective glutaraldehyde is. Once inside the formation, dilution of all biocides will occur and a less than lethal dose of biocide might result, reducing the killing efficacy, especially at the outside edge of the treatment zone.

Some oil and gas operators specify only glutaraldehyde and skip the on-the-fly oxidizing biocide step to save money, though eliminating the oxidizing biocide typically conserves less than 1% of the total well completion cost. This savings could be offset by production chemical maintenance costs over the life of the well. Whereas, some operators use only chlorine dioxide or other oxidizing biocide and skip the addition of glutaraldehyde or other non-oxidizer at the sand hopper.

Chlorine dioxide is an unstable gas and must be generated onsite as it is needed. Chlorine dioxide generators must feed and mix precursor chemicals (acid, bleach, and sodium chlorite solutions) and provide sufficient residence time for the chlorine dioxide reaction to go to completion. The required residence time varies from less than a minute to 15 minutes depending on the chemistry selected. Commercial ClO₂ generators differ predominantly in the type of chemical feed systems they employ. Three types of designs are used: 1) vacuum feed systems which pull fluids into the generator; 2) pressure feed systems which push fluids into
the generator; and 3) a combination of pressure and vacuum feed systems. Selection of an experienced ClO₂ service provider is critical because chemistry is complex and it is difficult to obtain proper dose control without a thorough understanding of chemistry.

**The Economics of Fresh Water versus Treatment of Produced Water**

It is generally economical to recycle flowback and produced water if continuous fracking activity is occurring within +/-20 miles of a water storage system. It is not economic during a downturn when fracking activity is low and fresh water is readily available, or when SWD disposal is abundant and inexpensive. Some illustrative figures for the Permian Basin are shown below based on the market knowledge of the authors.

| Fresh Water Purchase, Transportation, Treatment and Disposal Costs, $/bbl |
|---|---|
| Cost, $/bbl | Description |
| 0.30 - 0.50 | Fresh water price at source in the Midland Basin; higher in the Delaware |
| 0.20 - 1.00 | Truck and surface hose transportation, depending on distance and transportation mode |
| +/- 0.10 | Frac water treatment cost on-the-fly |
| 0.20-3.00 | Transportation of produced water and flowback to SWD well, depending on distance and transportation mode |
| +/- 0.75 | SWD injection cost (higher in the Delaware) |
| **1.55 – 5.35** | Total untreated water cost |

| Water Recycling Cost, $/bbl |
|---|---|
| Cost, $/bbl | Description |

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<th>Cost, $/bbl</th>
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<td>0.00 – 4.10</td>
<td>Untreated water cost minus recycled water cost</td>
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Water purchase, transportation, storage, treatment and disposal costs vary widely depending on source locations, shipping distances, modes of transportation (trucks are the most expensive while permanent buried pipelines are the least expensive), quantities and quality of water treated, whether or not in-ground water impoundments are allowed by regulation and can be cost-justified, and the proximity of SWDs. While the cost savings from recycling waste water can be significant, the real issue is what to do with all of the formation water produced over the life of the wells in the oilfield. The industry is working on solutions, but their implementation could be years away.

**Market Trends and Conclusions**

Regarding near term trends, Simmons & Company reported that pressure pumping and proppant demand have been increasing since the bottom of the down-cycle in the second
quarter of 2016, and prices have increased by 20+%.\textsuperscript{15} Frac water demand should track pressure pumping and proppant demand, and pricing should eventually follow. Much excess pressure pumping capacity has been removed from the market simply by not replacing the attrition of capacity caused the normal wear and tear of the pressure pumping operation (slick water fracs are equivalent to sand blasting the inside of the pumps and other equipment used in the pressure pumping operation, while gel fracs are only somewhat less punishing on the equipment). Proppant capacity can be rationalized by the depletion of existing sand mines and the absence of new mine development. Excess water treatment capacity is harder to rationalize because it does not deteriorate or deplete to the same extent as pressure pumping equipment and proppants. However, it is not unreasonable to assume that some of the highest cost, largest footprint treatment capacity will not return to the market.

Regarding longer term trends, the number and length of laterals being horizontally drilled and fracked have been growing and could continue to grow and thereby increase the amount of water, proppants and pressure pumping capacity required per frac. The amount of water consumed in a frac was around 100,000 barrels a few years ago and is as high as 500,000 barrels today.

Chlorine dioxide and most oxidizing biocides are considered “green” chemicals because they remove bacteria, H\textsubscript{2}S, metals and other impurities rapidly and effectively and then breakdown into components that are considered to be “Generally Recognized as Safe” (“GRAS”) by government authorities. In contrast, non-oxidizing biocides which are more persistent in the environment are not considered “green” solutions because these organic compounds are stable and resist breakdown into benign components. The EPA released a report on December 13, 2016, “7th Annual Private Company Energy Conference Recap.”

\textsuperscript{15} Simmons & Company report on December 18, 2016, “7th Annual Private Company Energy Conference Recap.”
2016 announcing that there is not enough data to conclude that hydraulic fracturing poses a risk to water supplies and the environment. Nevertheless, some people are concerned that the fracking process involves the use of chemicals that could contaminate water used in human and animal consumption. It is true that some of the frac chemicals are hazardous, however, only small quantities of these products are used. More importantly, fracs occur a great distance below the water table. Properly designed wells pose little or no risk to the environment, but the use of oxidizing biocides in place of non-oxidizing biocides would be a risk mitigator.

Most produced water must be disposed by injection into salt water disposal wells. Produced water occurs naturally and should not pose an environmental risk if it is returned to the earth into the same formation from which it originated at a point near where it was removed and reinjected into a properly designed disposal well at a safe injection rate. However, if water is injected at an excessively high rate, it could trigger seismic activity in certain earthquake prone regions. The treatment and recycling of produced water is a partial mitigator to this risk. Tightening environmental regulations that do not curtail fracking activity should generally be favorable to the water treatment industry that uses oxidizing biocides.

In conclusion, the near and long term trends in the water treatment industry are positive. Efforts are underway to treat a greater percentage of produced water and to build out the pipeline, storage and treatment infrastructure, continuing to improve the economics of water treatment and logistics. The costliest problem is the removal of dissolved salts. The oil and gas industry cannot justify the cost of salt removal, but certain applications that command higher water prices possibly can.

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16 “If the EPA can’t do it, who can?,” Houston Chronicle, December 17, 2016, p. B1.