**Water Treatment Technologies: Converting Frac Flowback and Produced Water into a Reusable Resource**

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## Introduction

Shale gas exploration is steadily increasing in the United States and around the world. Unconventional drilling with horizontal wells and multiple-stage fracturing is the most prevalent mode of gas extraction offering maximum productivity and cost efficiency. Hydraulic fracturing of a well encompasses, on the average, 12 fracturing stages each using approximately 10,000 to 12,000 bbl of water per stage. As shale gas exploration increases, water usage in the main U.S. shale plays is projected to increase from about 450 million bbl in 2010, to around 675 million bbl by the end of 2015. (Cap Resources, Internal Market Study, November 2010)

The need for such vast amounts of water in hydraulic fracturing operations significantly affects water availability and sourcing for all uses, and also the cost and logistics in accessing and trucking the water to points of use or disposal sites. Furthermore, regulations designed to protect communities and the environment from potential sources of contamination, are becoming increasingly stringent.

Approximately 10% to 30% of the hydraulic fracturing water injected returns to the surface as so called flowback water, along with various amounts of produced water which will continue to emerge during the lifetime of the well. In the interest of conservation and sustainability, it is highly desirable to maximize any opportunities to reuse the flowback water and to use some of the produced water in subsequent drilling and fracturing operations. Recycling and reuse for other drilling and fracturing jobs has many benefits, including reduced fresh water use, reduced $CO_2$ footprint and overall environmental impact, reduced volume of transportation, and ultimately less cost.

To this end companies specializing in water treatment continue to develop fit-for-purpose on-site means of treating flowback water (FBW) and produced water (PW). Currently there are relatively wide variations in target specifications for recycled water, depending on use requirements, location and formation characteristics. Similarly regulations for water sourcing, use, reuse and disposal tend to vary widely over state and regional boundaries. Consequently a host of new technologies are being developed and implemented to address specific requirements in a cost-effective and technically efficient manner.

Typical FBW/PW recycling challenges for use in hydraulic fracturing include solids and oil removal, softening or scale minimization, disinfection and desalination. Approaches include mechanical and chemical precipitation, filtering devices, absorption media, cross-flow membrane technologies, and various bacterial disinfection methods based on ozone, chlorine compounds and ultraviolet light. This paper provides a brief overview of waste water recycling technologies used in the Oil and Gas industry and illustrations and discussion of methods currently employed.

**Produced Water Background**

One of the major issues associated with development of natural gas fields in North America is management of the produced water and frac flowback water. Countless strategies exist and new equipment vendors seem to materialize daily promising that theirs is the solution to all of the producer's water problems. Since water qualities vary significantly from one shale play to the next and other factors including climate, topography, geology, availability of power, chemicals, landfills, operational limitations, environmental regulations and various other issues, all affecting the optimal solution, one must step back and take a comprehensive and long term view in order to plan and engineer the proper water management system.

This briefing will discuss general strategies for managing parameters of concern, along with a focused discussion concerning the technology currently being deployed.

**Customer Requirements**

There are a few distinct categories that summarize the needs of Oil and Gas industry customers in regards to water treatment options. Key treatment approaches can be divided into the following four types:

Type 1: Total Suspended Solids (TSS) and Bacteria
Type 2: Hardness (Softening) and Oil and Grease
Type 3: Total Dissolved Solids (TDS) - Mobile
Type 4: Total Dissolved Solids (TDS) - Central Facility plus Conveyance System

**<u>Type 1: Total Suspended Solids (TSS) and Bacteria</u>**

TSS Removal:

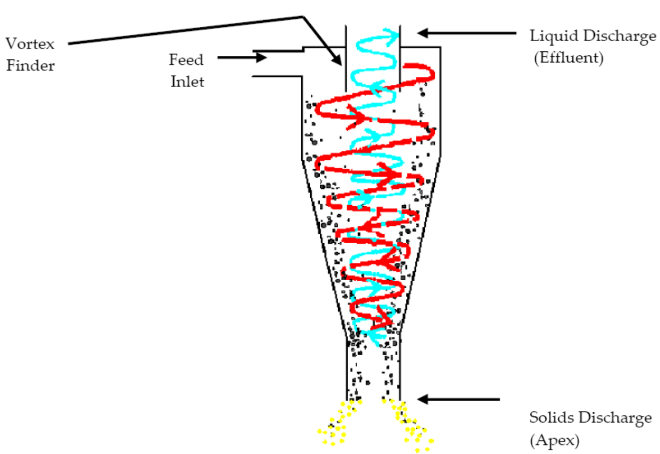
Total Suspended Solids (TSS) is generally managed by settling/sedimentation systems using coagulants and flocculants, filtration or hydrocyclones. Based on current operational experience, filtration systems are the most efficient and practical means for TSS removal for land-based operations. For offshore applications, hydrocyclones are an excellent choice where space is limited for both equipment and consumables.

The predominant method deployed by land-based operations for the removal of TSS focuses on the implementation of basic sock and/or cartridge filtration, depicted in Figures 1 and 2. Typical daily throughputs are in the 5,000 to 10,000 bbl/day range. Sock and cartridge filtration has proven to be the most cost effective and reliable means of treatment. Advantages of this system are simplicity of design and a relatively small footprint. Disadvantages of sock and cartridge filtration are that these systems tend to be rather labor intensive, often requiring large amounts of consumables. However, system and labor costs are minimal compared to more rigorous treatment options. Due to its relative compactness, this technology lends itself well to both mobile land operations and offshore applications.

Figure 1 – Filtration Pods


Figure 2 – Typical Mobile Filtration Trailer

The predominant method deployed by offshore operations for the removal of TSS focuses on the use of hydrocyclone solids removal technologies. In its basic layout a hydrocyclone consists of a conically shaped chamber. Water is introduced tangentially under pressure into the wider end of the chamber creating a vortex. Moving downwards through the narrowing vessel, the rotational velocity of the water increases, forcing the more dense material (solids) toward the outer wall. The less dense material (water) is concentated in the center. The end effect is that the solids are forced though the apex of the chamber, while the liquid exits at the wider end. These devices lend themselves to direct processing of produced water for solids without the size and bulk of traditional pretreatment technologies. Illustrations are presented in Figures 3 and 4.




**Drilling Fluids Processing Handbook, ASME Shale Shaker Committee, 2005.*

Figure 3 - Hydrocyclone Schematic

Figure 4 - Hydrocyclone Cutout View

Bacteria Control:

Bacteria removal or disinfection can be accomplished by various technologies using ultraviolet light, ozonation, the addition of chlorinated compounds, or by the use of chemical bactericides. Methods currently used by field operations include ozonation and chlorine dioxide generation and injection at the treatment site. These two on-site generation technologies allow minimal chemical transportation and are showing the most promise as clients commonly prefer 'bactericide free' control.

During the ozonation process, ozone is generated from air through an ozone generator. Ozone concentrations as low as 0.5% to 3% have been shown to accomplish flowback water disinfection meeting or exceeding the desired goal of 1,000 cfu/mL (cfu = colony forming units). Test assays conducted in conjunction with 200 gal/min process flow rates, include heterotropic plate count (HPC), acid producing bacteria (APB), and sulfate reducing bacteria (SRB). The mechanism by which ozone compromises bacteria growth is based on rupturing the cell membrane, resulting in cellular fluid leakage and imbalances leading to functional shutdown of the cell.

Chlorine dioxide acts on bacterial cell membranes in a conceptually similar manner to ozone. The effectiveness of chlorine dioxide in our experience has been similarly compelling when compared to ozone disinfection, based on the same types of bacteria testing. Chlorine dioxide is produced on site by electrolytic conversion of sodium chlorite. Field testing of flowback and produced water has been conducted at up to approximately 500 gal/min flow rate with effective chlorine oxide concentrations as low as 10-30 ppm.

**Type 2: Hardness (Softening) and Oil and Grease (Emulsions)**

Hardness Removal:

Hardness is a description of the concentration of scale forming ions present in the water. In produced and frac-flowback waters, the most prevalent elements of concern are Ca, Mg, Fe, Sr, and Ba. These ions are commonly removed by lime softening, ion exchange, or nanofiltration.

The predominant method deployed by our operations is cold lime softening, involving the addition of lime, i.e. $Ca(OH)_2$, to the water where it dissociates into $Ca^{2+}$ and $OH^-$ ions eventually forming calcium carbonate. The calcium carbonate is very insoluble compared to lime resulting in the precipitation responsible for reducing the calcium concentration in water. Figures 5, 6 and 7 illustrate cold lime softening operations, with Figure 8 summarizing some typical results.

Figure 5 - Field View

Figure 6 - Mixing Tanks

Figure 7 - Chemical Feed

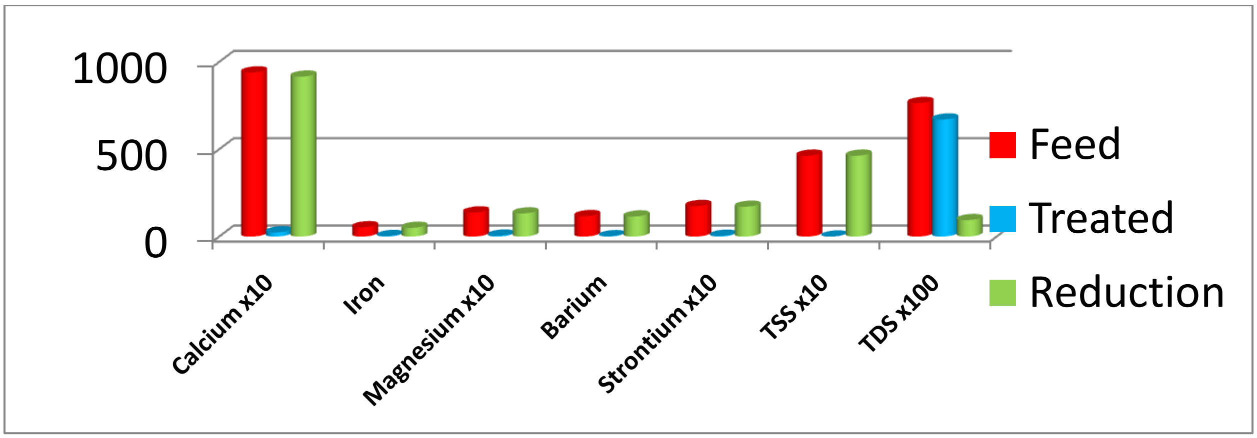



Figure 8 – Concentrations Before and After Treatment

Oil and Grease:

Oil and grease (O&G) may be present in produced water in free, emulsified or soluble forms. The bulk of the total O&G entrained in the water can be extracted using a variety of mechanical devices including hydrocylones, dissolved air flotation (DAF) systems, and specialized media filters containing porous hydrophobic absorptive substances. These basic approaches remove free oil, whereas added chemical treatment (de-emulsifiers or gas injection), is typically needed to remove trace amounts of emulsified or dissolved material. Specialized absorptive media is also very effective in this regard without the need for adding chemicals.

The predominant method deployed by our operations utilizes compact flotation. This technology combines the concepts of hydrocyclone and gas flotation, by injection of nitrogen. During this process, minute oil droplets are made to agglomerate and coalesce, facilitating separation from the water. The separation process is aided by baffles inside the chamber and a gas flotation effect is caused by the release of residual gas from the water. Flocculants can be added for enhanced performance. The separated oil and gas is removed continually via an outlet pipe at the top of the vessel.

Single-step separation has proven to reduce the oil-in-water (OiW) content to below 20 mg/L, while simultaneously degassing the water. Two compact flotation units (CFU) in series have achieved OiW contents below 10 mg/L. The benefits of this technology are that it can handle large volumes of water within a small equipment footprint. Compact flotation therefore is highly suited for offshore use. As an example a 528-gallon vessel can treat water at throughputs of 1570 bbl/hr, or 26 bbl/min. A functional layout of the compact flotation process is depicted in Figure 9.

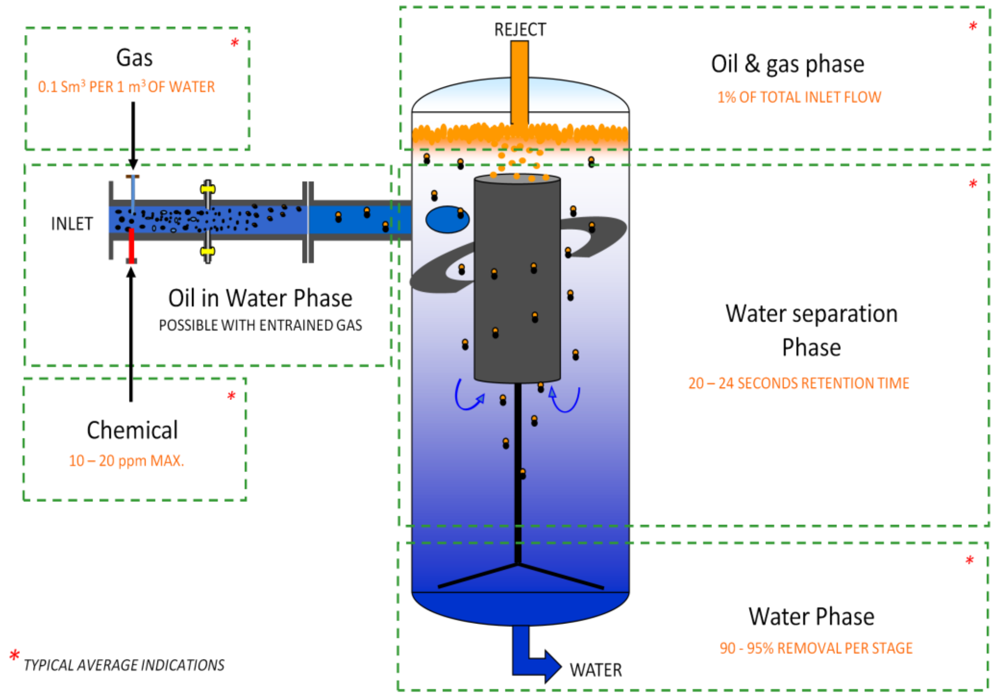



Figure 9 – Compact Flotation Unit

**<u>Type 3: Total Dissolved Solids (TDS) Removal - Mobile</u>**

Total Dissolved Solids (TDS):

Total Dissolved Solids are all particles that are less than 0.45 microns in size which include macromolecules, polymers, and both multivalent and monovalent ions. Removal of these species can be accomplished by either membrane filtration (micro-, ultra-, nano-filtration and reverse osmosis) or thermal technologies (distillation/evaporation). TDS removal methods are being deployed worldwide in produced water and seawater desalination, mostly in centralized systems, and in some cases in movable or mobile versions. Membrane treatments typically result in water salinities similar to drinking water, or less than 1,000 mg/L, commonly with capabilities down to 500 mg/L.

The current method deployed by our operations utilizes an integrated tri-modular 10-gal/min mobile reverse osmosis (RO) system for on-site flowback water desalination. The system consists of three 30-ft containers providing for pre-treatment utilizing chemical flocculation, clarification, and oil removal (Module 1), cold lime softening (Module 2), and micro-, ultra-, nano-, and reverse osmosis (RO) membranes (Module 3). The equipment is being used as a platform for evaluating different water qualities, exploratory treatment options, and for determining the optimal design of a commercial RO system. Views of the 10-gal/min modular unit are shown in Figures 10, 11 and 12.

Figure 10 - Module 2

Figure 11- Module 1

Figure 12
Reverse Osmosis

**<u>Type 4: Total Dissolved Solids (TDS) Removal – Central Facility plus Conveyance System</u>**

Centralized TDS treatment facilities typically are constructed when two conditions exist: Produced water volumes exceed potential reuse capacity; and low-cost transportation and disposal options are scarce. The primary costs associated with centralized treatment facilities revolve around two key components: treatment and transportation.

Centralized TDS treatment of produced water combines many of the pre-treatment steps previously discussed in combination with a membrane system. These facilities generate discharge quality water on a much larger scale. The basic pretreatment features including TSS, O&G, and hardness removal are typically required prior to reverse osmosis or other membrane treatments.

In addition to the challenges of developing a larger, permanent facility to manage the TDS treatment of produced waters, planning and designing of conveyance systems are equally important (similar to the movement of products in and out of a petrochemical manufacturing plant). A key operational decision is to determine the optimal mode of conveyance of the water to be treated and discharged. In the long term, trucking almost always proves to be the most expensive option to transport water. Even though pipeline networks initially require substantial capital to construct, the long term savings are often significant when compared to trucking. In addition, pipeline conveyance is a much 'greener' alternative to trucking, minimizing exhaust pollution, and degradation of road infrastructure due to large volumes of truck traffic. Once the necessary transportation infrastructure has been established, centralized facilities have a clear advantage in reducing overall transportation and treatment costs.

**Summary**

As shale gas exploration is steadily increasing in the United States and around the world, understanding the basic water treatment and management strategies is crucial to the success of any unconventional shale gas production operation. Recycling and reuse of flowback and produced waters for drilling and fracturing jobs has many financial and environmental benefits. These include a reduction in: demand of fresh water sources; in trucking and disposal volumes; and in $CO_2$ footprint and overall environmental impacts. In addition to the environmental benefits, when implemented properly, these strategies will lead to significant reductions in overall operational costs. Produced water is the only drought-resistant form of water available to our ecosystem. Management of this resource is crucial to operational and ecological sustainability.