EPA Hydraulic Fracturing Workshop 1
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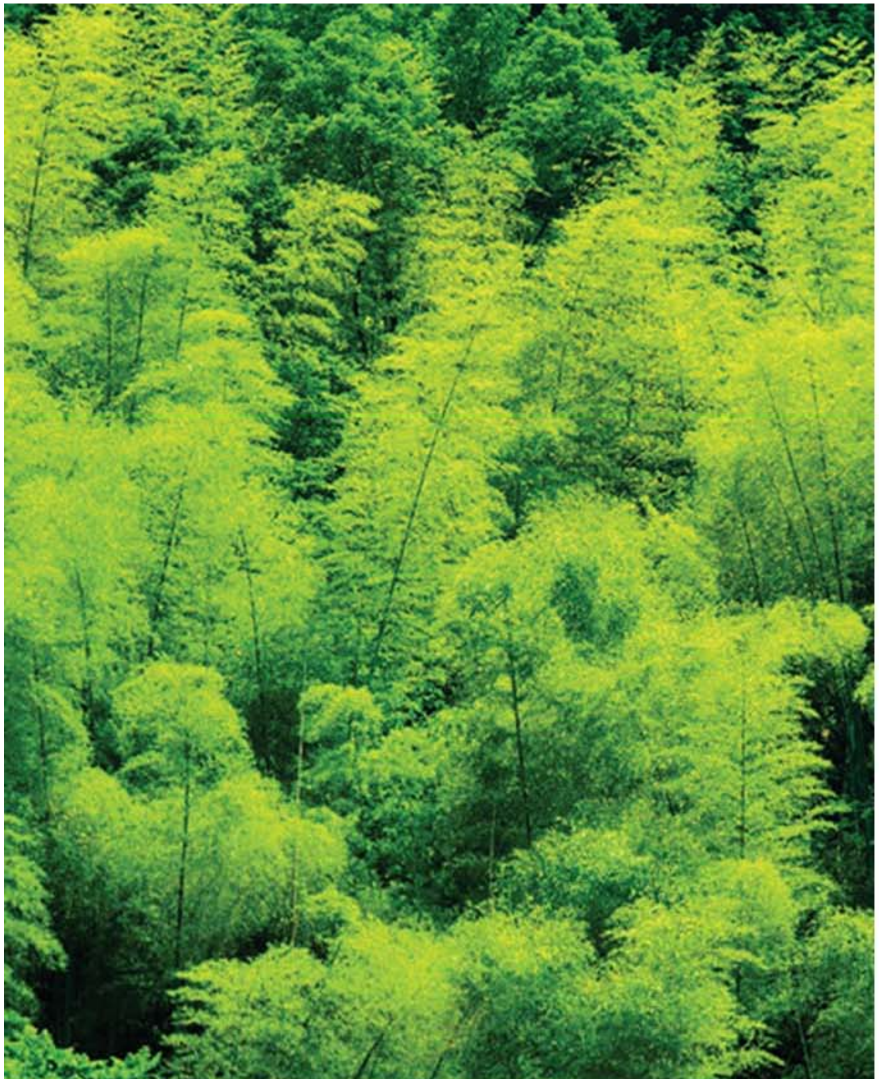
NATURAL GAS: FUELING AMERICA'S FUTURE



High Rate Hydraulic Fracturing Additives in Non-Marcellus Unconventional Shales

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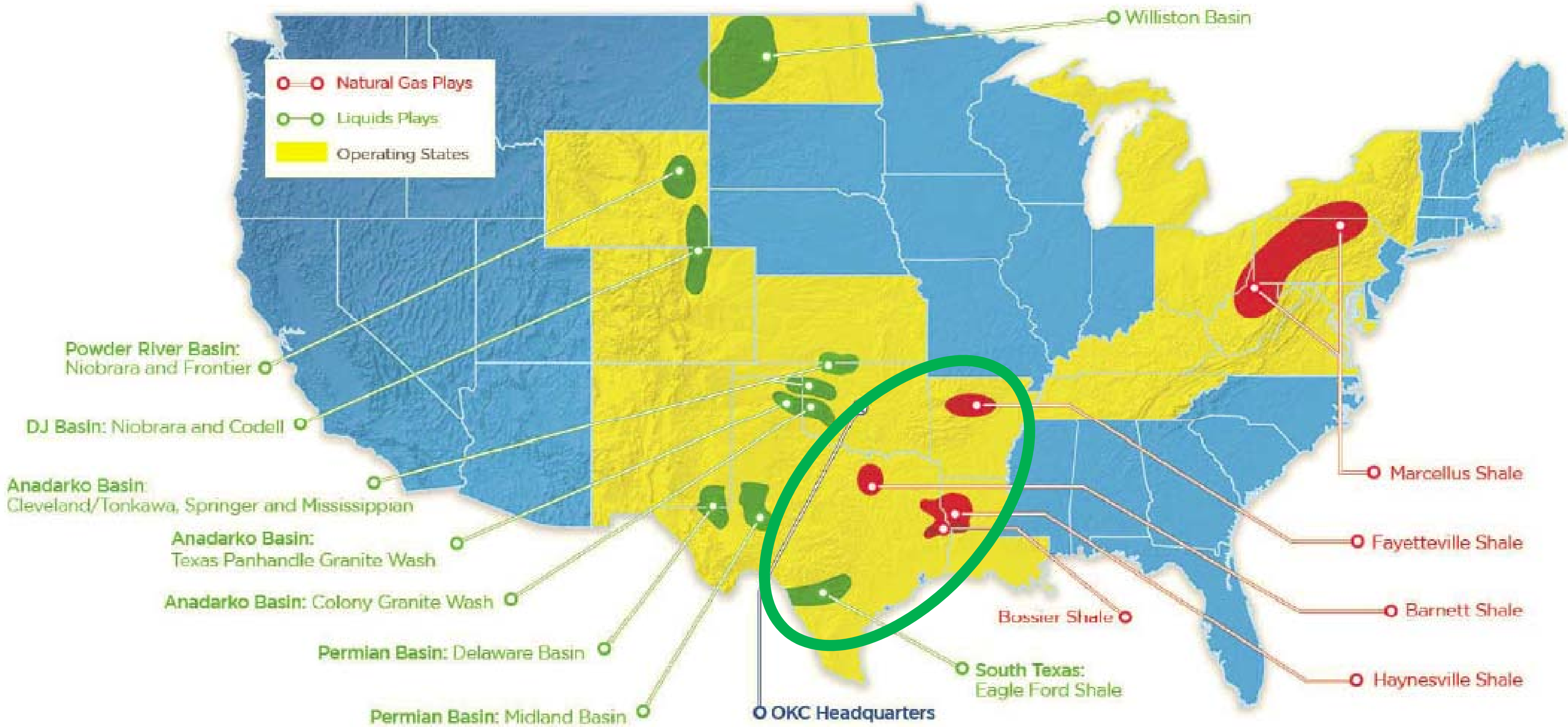
Agenda

- Non-Marcellus Unconventional Shales
- Typical Additives by Play
- Recent Trends in Additive Selection
- Key Points

Unconventional Shale Plays



Shale Information

Shale Play	Fayetteville	Barnett	Eagle Ford	Haynesville
Average Depth From Surface (ft)	4,500	7,400	9,000	11,500
Bottom Hole Temperature (F)	130	190	260	320
Bottom Hole Pressure (psi)	2,000	2,900	6,200	10,000

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- Non-Marcellus Unconventional Shales
- Typical Additives by Play
  - Purpose, Chemistry and Concentration
- Recent Trends in Additive Selection
- Key Points

Historical Additives by Play (non-MS)

Additive	Barnett	Fayetteville	Haynesville	Eagle Ford
Friction Reducer	X	X	X	X
Biocide	X	X	X	X
KCl Substitute	X	X	X	X
Scale Inhibitor	X	X	X	
Surfactant	X	X	X	X
Hydrochloric Acid*	X	X	X	X
Gel	X		X	X
Cross-linker			X	X
Breaker	X		X	X

* - includes acid corrosion inhibitor and iron control

Friction Reducer

- **Purpose**
  - *Reduces surface tension between fluid and pipe surface and helps to maintain laminar flow.*
- **Chemistry**
  - Polyacrylamides
  - Typically dispersed in a hydrocarbon carrier
  - Anionic (most common) and cationic (less common)

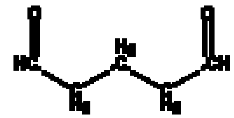
- **Use Concentration**
  - 500 – 1,000 ppm
  - 0.05 – 0.1% of total fluid pumped (v/v)

Biocide

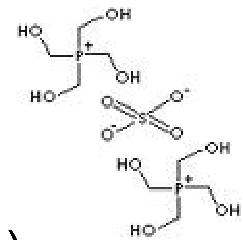
- **Purpose**
  - *Sanitizes treatment fluid to reduce or eliminate bacteria presence.*
  - *Bacteria can*
    - *prevent gels from functioning*
    - *Create corrosion failures in downhole and surface equipment*
    - *Create hydrogen sulfide (H_2S) gas which is another source of corrosion*

Biocide

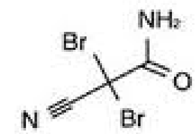
- **Chemistry**
  - Glutaraldehyde



  - Glut / quaternary amine blends
  - THPS (tetrakis hydroxymethyl phosphonium sulfate)



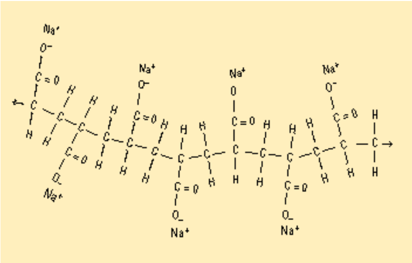
  - DBNPA (2,2-dibromo, 3-nitriloproprionamide)



  - Sodium hypochlorite (NaClO)
  - **All products are regulated under FIFRA and must be registered with the EPA and the States**
- **Use Concentration**
  - 75 – 500 ppm
  - 0.075 – 0.05% of total fluid

Scale Inhibitor

- **Purpose**
  - *Prevents mineral scale formation as the stimulation fluid mixes with formation water or after dissolving existing mineral salts in the reservoir.*
- **Chemistry**
  - Polymers (most common)
    - — carboxylic acid
    - — acrylic acid
  - Phosphonates (less common, many incompatible w/ other additives)



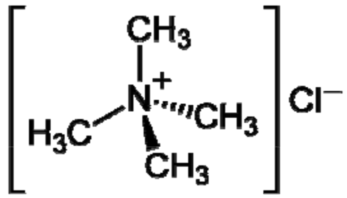
- **Use Concentration**
  - 75 - 120 ppm
  - 0.075% – 0.12% of total fluid pumped

Potassium Chloride (KCl) Substitute

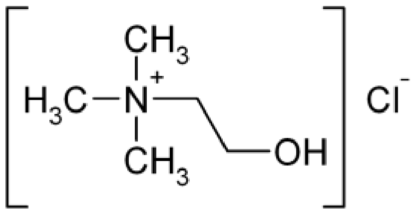
- **Purpose**
  - *Prevents the swelling of water sensitive clays*
  - *Type and amount of clays can vary from shale to shale*
  - *Drill cuttings and core analysis used to quantify*
  - *Capillary suction time (CST) testing used to determine sensitivity to low salinity water*

Potassium Chloride (KCl) Substitute

- **Chemistry**
  - Historically, quaternary amines
    - —Tetramethylammonium chloride (TMAC)
  - Last year, move to choline chloride
    - —Commonly found in animal feed
    - —Also as a nutritional supplement for humans
- **Use Concentration**
  - 500 – 2,000 ppm
  - 0.05% - 0.2% of total fluid pumped



TMAC



Choline Chloride

Surfactant

- **Purpose**
  - *Reduce interfacial tension in the formation and promote more robust water recovery after hydraulic fracturing*
  - *Prevent emulsions in shale plays containing significant amounts of oil, water and gas*

Surfactant

- **Chemistry**
  - Variety of formulations
    - —Typically anionic, non-ionic or amphoteric
    - —Simple laurel sulfates to more complex fluoro- and nano-surfactants
- **Use Concentration**
  - 500 – 1,000 ppm
  - 0.05% - 0.1% of total fluid pumped

Hydrochloric (HCl) Acid

- **Purpose**
  - *Dissolves contaminates in casing.*
  - *Dissolves acid soluble minerals that may be present in the shale*
- **Chemistry**
  - Typically 15% active
  - Rapidly reacts with iron and minerals that may be present in the shale

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2\uparrow$$

Hydrochloric (HCl) Acid

- **Use Concentration**
  - Dependent on:
    - —Perf clusters / well
    - —Mineral composition of shale
  - Typical volumes
    - — 0.08% - 2.1% of total fluid pumped (as acid volume)
    - — 0.012% - 0.31% of total fluid pumped (<u>as active acid</u>)

Acid Corrosion Inhibitor

- **Purpose**
  - *Reduces corrosive attack on bare steel*
- **Chemistry**
  - Complex Assortment
    - Formic acid
    - Amines, amides, amido-amines
- **Use Concentration**
  - Dependent on bottom hole temperature and exposure time
  - 2,000 – 5,000 ppm of acid volume
  - 0.0004% - 0.0043% of total fluid pumped

Iron Control

- **Purpose**
  - *Prevents precipitation of any dissolved iron as acid reacts and spends*
- **Chemistry**
  - Citric acid
  - Acetic acid
  - Thioglycolic acid
  - EDTA
- **Use Concentration**
  - 5,000 ppm of acid volume
  - 0.0004% – 0.011% of total fluid pumped

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Green Frac™

- Initiated in 2009
- Primary Drivers:
  - Minimize Risk of Exposure To Workers During Hydraulic Fracturing Activities
  - Minimize Environmental Impact of Surface Spills
- Evaluate – Eliminate - Replace

Green Frac Status

Additive	Barnett	Fayetteville	Haynesville	Marcellus	Eagle Ford
Friction Reducer	GF* Test	GF Test	GF Test	GF Test	GF Test
Biocide	GF Test	GF Test	GF Test	GF Test	GF Test
KCl Substitute	Eliminated	GF Substitute	GF Substitute	Eliminated	GF Substitute
Scale Inhibitor	GF Test	GF Test	X	X	
Surfactant	Eliminated	Eliminated	Eliminated	GF Test	X
Gel	X		X	Occasional	X
Cross-linker			X		X
Breaker	X		X	Occasional	X
HCl	X	X	X	X	X

* - Green Frac™

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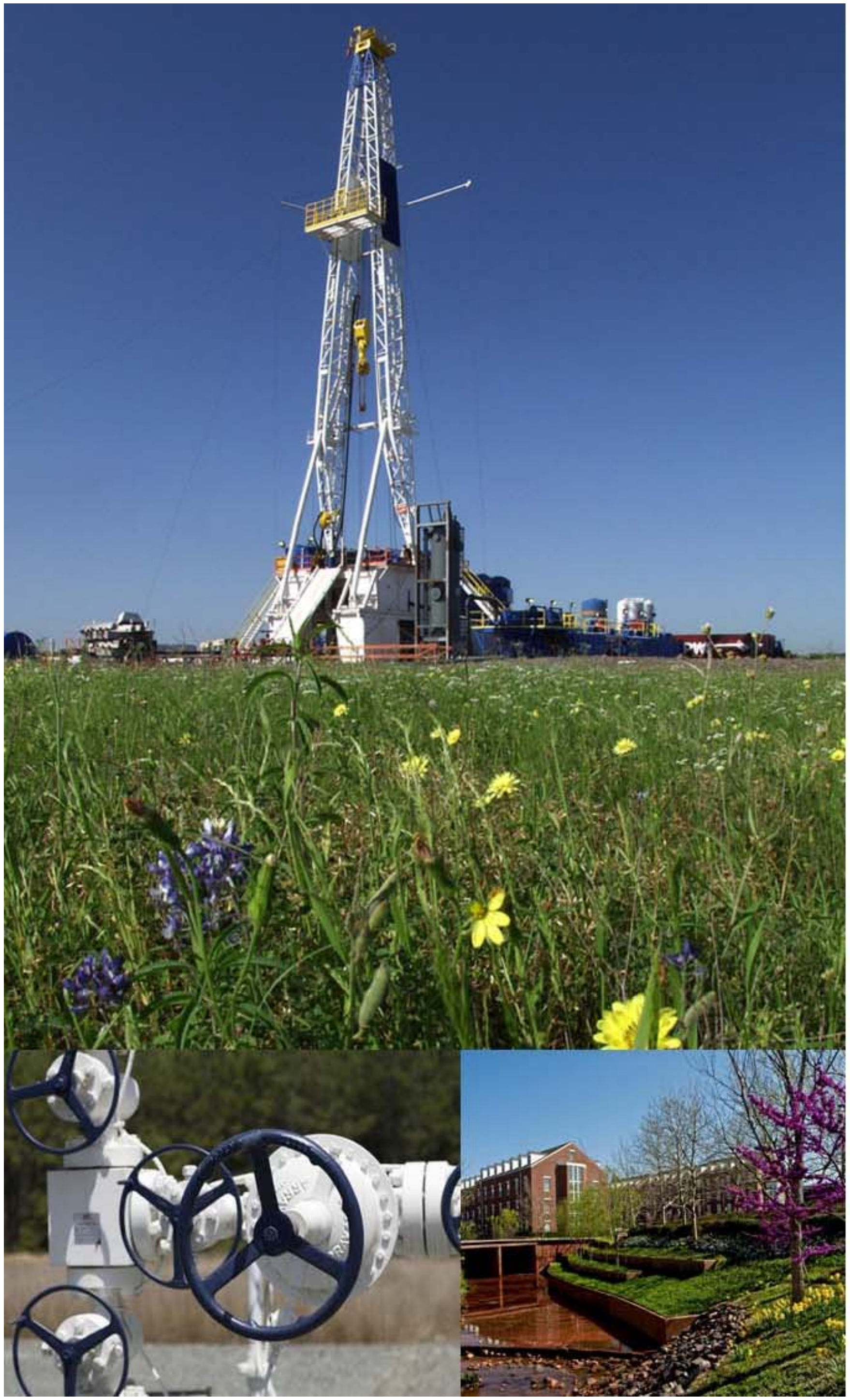
Key Points

- *Hydraulic fracturing fluids do not contain 596 toxic compounds.*
- *Chemical additives account for <1% of the total fluid pumped during the majority of hydraulic fracturing activities.*
- *Chesapeake's Green Frac™ program has eliminated or found more environmentally friendly alternatives for ¾ of the additives historically used in hydraulic fracturing.*



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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Introduction

In a sister publication presented during this workshop, another operator discussed the use of hydraulic fracturing additives in the Marcellus Shale. To avoid unnecessary repetition, this paper will focus on additives used in four other major U.S. unconventional shale plays – the Barnett Shale located in North Texas, the Eagle Ford Shale located in South Texas, the Fayetteville Shale in Arkansas and the Haynesville Shale that lies beneath East Texas and Northwestern Louisiana. The additives used in each play will be discussed, along with comments regarding why they are used, the general chemistries involved with each and the normal usage range in fracturing fluids. Finally, a discussion of the recent trends in the selection of additives will be discussed.

Non-Marcellus Unconventional Shales

Of the four unconventional shales listed above, all are traditional gas plays with the exception of the Eagle Ford. Depending on location, a well in the Eagle Ford can produce gas, gas and condensate or gas and oil. The table below illustrates some comparable physical data for the four shales.

Table 1. Physical data for four shales

Shale Play	Fayetteville	Barnett	Eagle Ford	Haynesville
Average Depth From Surface (ft)	4,500	7,400	9,000	11,500
Bottom Hole Temp (F)	130	190	260	320
Bottom Hole Pressure (psi)	2,000	2,900	6,200	10,000

Of the four, the Fayetteville is the "shallowest" with an average depth of slightly less than one (1) mile beneath the surface of the Earth. On the opposite end is the Haynesville which, on average, can be found more than two (2) miles beneath the surface. As such, these formations are separated from drinking water aquifers by thousands of feet of multiple geologic strata. Often, temperature and pressure increase with depth and that is seen in the data above. The Fayetteville has the lowest bottom hole temperature and pressure and the Haynesville the highest. Temperature has to be taken into account when selecting additives and concentrations for hydraulic fracturing applications.

Typical Additives

In many articles published in various media over the last few years, the number of additives used in hydraulic fracturing is often grotesquely over-stated. In a recent documentary, a statement was made claiming that hydraulic fracturing fluids could contain as many as "596 toxic compounds". Some hydraulic fracturing activities may use as many as 11 additives, but many times the procedures contain far fewer than that. The 11 that may possibly be used are: friction reducer, biocide, scale inhibitor, potassium chloride (KCl) substitute, surfactant, hydrochloric acid, acid inhibitor, iron control agent, gel, cross-linker and breaker (linear and cross-linked gels, along with a few additives that are occasionally required in these fluid systems, will be discussed by another author and will not be discussed in this paper). Following are the purpose, typical chemistry and use concentrations for each additive.

Friction Reducers

This is the product responsible for the term "slick water". Friction reducers are used to reduce interfacial tension between the fluid and the contact surface of the steel pipe the fluid is being pumped through and to maintain laminar flow while pumping. Maintaining laminar, or non-turbulent, flow is critical to achieving the fluid injection rates necessary for hydraulic fracturing of unconventional formations, including shales. The active ingredient in friction reducers is typically a medium to long chain polyacrylamide. When injected into fresh water, the polyacrylamide hydrates and uncoils and prevents turbulent vortices in the moving water. An average usage rate for most friction reducers is 500 to 1,000 parts per million (ppm) and they are injected throughout the entire fluid. On a total fluid basis, they typically account for 0.05% - 0.1% of the total fluid volume pumped.

Biocides

The source water that makes up 99+% of the average hydraulic fracturing stimulation often contains varying concentrations of bacteria that have the potential of causing problems with the additives being used, the overall integrity of the wellbore and surface production equipment and can impart undesirable contaminants to the produced gas stream. Many bacteria can degrade the gels used for building fluid viscosity and have the potential to aggressively attack the metal equipment used both downhole and on the surface for producing natural gas and liquids from the well. Biocides are added to the source water to sanitize the fluid and greatly reduce the concentration of bacteria.

There are several chemistries utilized as biocides in hydraulic fracturing. Historically, glutaraldehyde and blends of glutaraldehyde have been used. Glutaraldehyde has been in use in several industries for many years and has a long history as a disinfectant for medical and dental equipment. Since the late 1990's, a product commonly referred to as THPS (tetrakis hydroxymethyl phosphonium sulfate) has been used in many areas because it degrades in the environment more rapidly that glutaraldehyde. Another product that is highly biodegradable is DBNPA (2,2-dibromo,3-nitriloproprionamide). There are some operators who use sodium hypochlorite (the active ingredient in household bleach) for sanitation of source waters. Regardless of the chemistry being used, it is important to note that all biocide usage is regulated by the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) and accordingly, each product must be registered for use by the U.S. Environmental Protection Agency (EPA) and by each State in which it will be applied. Biocides are commonly applied throughout the whole hydraulic fracturing fluid at a rate of 75 to 500 ppm and represent 0.075% - 0.05% of the total fluid volume.

Scale Inhibitors

Water used during the hydraulic fracture stimulation often has a potential of producing a mineral scale when coming in contact with naturally occurring water in the producing formation. Additionally, physical changes imparted on produced water (temperature, pressure, etc.) during initial production can cause mineral solids to precipitate from the fluid. To prevent this, Operators use a scale inhibitor injected throughout the hydraulic fracturing fluid. Owing to their compatibility with other fracturing additives, the most commonly used chemistries are carboxylic acid and acrylic acid polymers. Scale inhibitors are usually used at relatively low dosages throughout the frac fluid (75 to 120 ppm) and make up 0.0075% - 0.012% of the total fluid volume.

KCl (Potassium Chloride) Substitute

Most of the unconventional shales contain varying concentrations of water sensitive clays. These clays swell when contacted by fresh water and can potentially shut off flow paths. To prevent this, Operators historically mixed powdered potassium chloride (KCl) in their fresh water at the surface prior to pumping the water downhole. The KCl in the water prevented absorption by the water sensitive clays. With the advent of high volume stimulations of unconventional reservoirs, the process of manually mixing powdered KCl in surface tanks became cumbersome and research was conducted to identify substitutes for powdered KCl. Laboratory testing indicated quaternary amines could prevent adsorption of fresh water by coating the clay particles present in the shale. The most popular chemistry for this application was a product referred to as TMAC (tetramethylammonium chloride).

In 2009, Chesapeake Energy initiated a program focused on looking at the overall environmental footprint of hydraulic fracturing additives to determine if improvements were possible. One of the first targets of this effort was TMAC. Through extensive lab and field testing, a new product, choline chloride, was identified as a very suitable replacement. Choline chloride is commonly used as a nutritional supplement in animal feed, especially as a growth aid for young chickens and it is also used as a nutritional supplement for humans. Chesapeake now uses choline chloride in most areas where KCl substitutes are necessary in hydraulic fracturing activities. Average use concentration for choline chloride is 500 to 2,000 ppm or 0.05% - 0.2% of the total fluid pumped.

Surfactants

Surfactants have been historically used in hydraulic fracturing to reduce interfacial tension between fluid and the shale and between different phases of fluid. In the first instance, the desire is more robust initial water production from the well and in the second, the goal is the elimination of emulsions in shales containing oil and water. The term “surfactant” covers a multitude of products and those used in hydraulic fracturing can be as simple as a laurel sulfate (similar to the ones used in household shampoos) to complex fluoro- and nano-surfactants. Where used, surfactants are typically used at 500 to 1,000 ppm throughout the fluid which would account for 0.05% - 0.1% of the total fluid volume.

Hydrochloric acid

Hydrochloric acid (HCl) is not used throughout the fracturing fluid, but rather usually is used to lead the fluid for each stage. This is done to clear the production casing string of any debris and to dissolve near-wellbore acid soluble minerals present in the shale. Dissolving these minerals promotes additional flow paths for gas and/or oil to make its way to the wellbore and thus improving the production from the well. Calcite ($CaCO_3$), a mineral commonly found in unconventional shales, rapidly reacts with, and is dissolved by, hydrochloric acid. Once this reaction is complete, the only remaining by-products are a soluble calcium salt, water and carbon dioxide.

The hydrochloric acid used in hydraulic fracturing operations is usually 7.5% or 15% active. The amount used is dependent on the number of perforations (openings to the shale reservoir) per well and the mineral composition of the shale. For the major shale plays mentioned earlier, typical usage range is 0.08% - 2.1% of the total fluid pumped (as volume of 15% HCl). However, when looking at the active component, this would actually equal to 0.012% - 0.31% of the total fluid pumped.

Acid Corrosion Inhibitor

While it is desirable for hydrochloric acid remove debris from the production casing, Operators do not want the acid to degrade the integrity of the casing itself. To prevent this, an acid corrosion inhibitor is utilized throughout the entire acid volume. Acid inhibitors tend to be complex products as they are tasked with a protecting the steel casing without reducing the acid’s ability to dissolve iron oxides (mill scale) that is usually present on the surface of the pipe. Acid inhibitors tend to contain amines, amides and/or amido-amines and often contain formic acid as an intensifier for higher temperature applications. Usage rates can vary from 2,000 to 5,000 ppm in the acid only which equates to 0.0004% - 0.0043% of the total fluid volume.

Iron Control

As hydrochloric acid reacts with acid soluble minerals, such as calcite, in the formation and “spends” there is a possibility for any iron oxide mill scale dissolved from the casing to precipitate. This precipitation could potentially block flow channels in the reservoir so iron control agents are used to prevent this from occurring. Iron control products are common organic acids such as citric acid, acetic acid, thioglycolic acid and EDTA (ethylenediaminetetraacetic acid) and incorporate the dissolved iron ion into their structures and prevent it from precipitating. Typical usage in nearly all applications is 5,000 ppm of the acid volume which equals 0.0004% - 0.011% of the total fluid volume.

Recent Trends in Additive Selection

Chesapeake Energy, the American Petroleum Institute and the American Natural Gas Alliance all feel strongly that the risk of contamination to groundwater from hydraulic fracture stimulation of deep shale unconventional gas is extremely miniscule. However, we do realize that there are employees who routinely work around hydraulic fracturing additives and while safety is paramount in our industry, there is always the potential for an accidental surface spill. It was with these two concerns in mind that we forged our Green Frac efforts.

As described above, Chesapeake Energy's Green Frac™ program was initiated in 2009 to determine if it was possible to improve the overall environmental "footprint" of the additives used in our hydraulic fracturing operations. Finding a substitute for the friction reducer, TMAC, was an early, and successful, target of our efforts. Moving forward from that point, Chesapeake has utilized our in-house laboratory, Geophysical, Engineering and Chemical assets to thoroughly evaluate the necessity of every additive in every play. A primary goal was to eliminate any additive that was not absolutely critical to successful completion and operation of our wells. For those we deemed critical, we sought out materials that posed lower risk to personnel and to the environment in the event of an accidental surface discharge. To date, we have either eliminated, have found more desirable substitutes or are in the process of successfully testing substitutes for the majority of additives historically used in hydraulic fracturing of unconventional shales.

Conclusions

- Contrary to what is often published in the media, the typical fluid used to hydraulically fracture an unconventional shale well does not contain "596 toxic compounds". Most frac stimulations contain fewer than eleven additives, including the corrosion inhibitor and iron control agent that is always included in the hydrochloric acid.
- Many of the additives we use are not 100% active. An example is hydrochloric acid which is typically used in a field strength of either 7.5% or 15% active ingredient. If we look at the activity of the various additives, you quickly see that the average hydraulic fracturing fluid contains less that 1% by volume of chemical components. 99% of the liquid volume is water.
- Chesapeake Energy is very proud of our Industry leading program, Green Frac™. Through this program, we have eliminated 20% of the additives used in our fracturing operations. In addition, we have identified and moved to more environmentally friendly substitutes (or have products successfully finishing field tests) for over half of the remaining additives.