Testing biocides in hydraulic fracturing

Overview

Hydraulic fracturing or ‘fracking’ is a process used in the oil and gas industry to enhance the productivity of an oil or gas well. It involves the fracturing of rock using water (mixed with sand and some chemicals) injected into a wellbore under high pressure and is commonly used in shale gas beds and other ‘unconventional’ sources of oil and gas.

Unconventional Oil and Gas Sources

Fracking is usually used in shale gas beds, tight oil/gas beds or coal seam gas beds. All are sources of oil or gas that are found in different types of rock formation and are typically difficult for an oil or gas drilling company to make economical without hydraulic fracturing. This is why it is referred to as a ‘well stimulation’ technique. Although the process has been used over the last 50 years, it has recently become prominent within the public debate due to the expansion of the technique in the US and concerns over the consequences of its widespread use.

Water Used in ‘Fracking’

The process of ‘fracking’ involves drilling a well bore deep underground, often with a horizontal stage used when a rock bed is particularly shallow. The rock is then fractured using explosives that create small fissures in the rock which aid the flow of oil and gas out of the bed into the wellbore. It is the low porosity of the rock that necessitates the hydraulic fracturing to make a well economical. Without hydraulic fracturing, the well would not produce enough oil and gas to make it worthwhile to drill.

Water, sand and some chemicals are injected down the well under pressure to ensure these fissures to stay open under the immense pressure caused by the rock formations above the target rock bed. It is the sand that holds the fissures open which are often just a few millimetres wide. A large amount of water (many millions of gallons) is used in a single frack and the water may come from many different sources, e.g. freshwater, saltwater or recycled water from a previous fracking process.
The chemicals that may be added to the water and the purpose behind their addition are listed in Appendix E of the EPA report into hydraulic fracturing from 2011. A summarized version can be found in table 4.

Figure 6 is taken from the EPA report into hydraulic fracturing, page 13.
Figure 7 is taken from the EPA report into hydraulic fracturing, page 13
Most of the chemicals added are those typically used in other industrial processes that utilise water and are added to maintain the integrity of the wellbore, e.g. surfactants, corrosion inhibitors, pH controllers and friction reducers.

Biocides are added to the water to prevent the build up of bacteria in the water that may lead to acid corrosion or the creation of sulphide based compounds. Bacterial growth can impair the production of oil and gas wells, and can be introduced into the fracking fluid from various sources including the source water and the proppant. Proppant is the term used for the sand (or other compounds) that hold the fissures open.

Table 4 lists the types of chemicals added to the water and its purpose. It is taken from the EPA report, page 29.

<table>
<thead>
<tr>
<th>Component/Additive Type</th>
<th>Example Compounds</th>
<th>Purpose</th>
<th>Percent Composition (by Volume)</th>
<th>Volume of Chemical (Gallons) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Deliver proppant</td>
<td></td>
<td>90</td>
<td>2,700,000</td>
</tr>
<tr>
<td>Proppant</td>
<td>Silica, quartz sand</td>
<td>Keep fractures open to allow gas flow out</td>
<td>9.51</td>
<td>285,300</td>
</tr>
<tr>
<td>Acid</td>
<td>Hydrochloric acid</td>
<td>Dissolve minerals, initiate cracks in the rock</td>
<td>0.123</td>
<td>3,600</td>
</tr>
<tr>
<td>Friction reducer</td>
<td>Polyacrylamide, mineral oil</td>
<td>Minimize friction between fluid and the pipe</td>
<td>0.088</td>
<td>2,640</td>
</tr>
<tr>
<td>Surfactant</td>
<td>Isopropanol</td>
<td>Increase the viscosity of the fluid</td>
<td>0.085</td>
<td>2,550</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td></td>
<td>Create a brine carrier fluid</td>
<td>0.06</td>
<td>1,800</td>
</tr>
<tr>
<td>Gelling agent</td>
<td>Guar gum, hydroxyethyl cellulose</td>
<td>Thicken the fluid to suspend the proppant</td>
<td>0.056</td>
<td>1,680</td>
</tr>
<tr>
<td>Scale inhibitor</td>
<td>Ethylene glycol</td>
<td>Prevent scale deposits in the pipe</td>
<td>0.043</td>
<td>1,290</td>
</tr>
<tr>
<td>pH adjusting agent</td>
<td>Sodium or potassium carbonate</td>
<td>Maintain the effectiveness of other components</td>
<td>0.011</td>
<td>330</td>
</tr>
<tr>
<td>Breaker</td>
<td>Ammonium persulfate</td>
<td>Allow delayed breakdown of the gel</td>
<td>0.01</td>
<td>300</td>
</tr>
<tr>
<td>Crosslinker</td>
<td>Borate salts</td>
<td>Maintain fluid viscosity as temperature increases</td>
<td>0.007</td>
<td>210</td>
</tr>
<tr>
<td>Iron control</td>
<td>Citric acid</td>
<td>Prevent precipitation of metal oxides</td>
<td>0.004</td>
<td>120</td>
</tr>
<tr>
<td>Corrosion inhibitor</td>
<td>N,N-dimethyl formamide</td>
<td>Prevent pipe corrosion</td>
<td>0.002</td>
<td>60</td>
</tr>
<tr>
<td>Biocide</td>
<td>Glutaraldehyde</td>
<td>Eliminate bacteria</td>
<td>0.001</td>
<td>30</td>
</tr>
</tbody>
</table>

Data are from GWPC and ALL Consulting, 2009, and API, 2010b.

* Based on 3 million gallons of fluid used.
Testing of Fresh Water Used in Hydraulic Fracturing

Of the chemicals added to the water, the main analyte that must be tested for on site before injection is the biocide. They are tested on site because of their inherent volatility which makes sampling and off site testing inappropriate.

Biocides that are commonly used include chlorine dioxide, chlorine, isothiazolone and glutaraldehyde. Again these are biocides often used in other industrial processes using water such as cooling towers.

The dosing rate of biocides is often automated using an in-line amperometric method which adds the biocide in controlled amounts depending upon the flow rate of the water being introduced to the well from the water source. A secondary off line method is usually carried out to calibrate the in line probe and as a check downstream of the injection point to ensure biocide is present in the correct concentrations in the fluid before it is finally injected in the wellbore.

Testing for biocides in the water can be challenging due in part to the growing trend of the use of recycled water to frack wellbores. More traditional colorimetric methods of testing (such as the DPD method for quantifying chlorine or chlorine dioxide concentrations) can be time consuming and difficult for engineers; they may not give consistent results where the water used is high in dissolved/suspended solids. Other methods such as ORP (oxidation-reduction potential) are user friendly but suffer from a lack of selectivity and often can’t be used as a quantitative tool.

There has been a growing trend within water treatment companies (who tend to be sub-contracted by the drilling company to manage the dosing of biocides into the water) to use new methods such as disposable amperometric sensors as utilised by the ChlordioXense. These methods have the advantage of being simpler to use and are not susceptible to inaccurate results as seen with colorimetric methods.
Testing of ‘Produced’ Water Used in Hydraulic Fracturing

Flowback water is the water that flows back to the surface during and after the completion of hydraulic fracturing. It consists of the fluid used to fracture shale and contains clays, the chemical additives, dissolved metal ions and total dissolved solids (TDS). The water has a murky appearance from high levels of suspended particles. Most of the flowback occurs in the initial stages of the fracking process while the rest can occur over a three to four week time period. The volume of recovery is generally less than half of the volume that was initially injected into the well. The rest of the fluid remains absorbed in the shale formation.

In contrast, ‘produced water’ is naturally occurring water found in shale formations that flows to the surface throughout the entire lifespan of the gas well. This water has high levels of TDS and metal ions such as calcium, iron and magnesium. It also contains dissolved hydrocarbons along with naturally occurring radioactive materials (NORM).

Historically, this wastewater from the fracking process was disposed of in large evaporation ponds. This however has now become socially unacceptable and the wastewater must be treated as industrial waste in the same way that water from other industrial processes is treated. The options available to water treatment companies involved in the oil and gas industry are either ‘direct injection’ into the ground to depths below the water table and between layers of impermeable rock, or the treatment and disposal of the water into surface water. Both methods often employ treatment of water with biocides.

Testing biocide concentration in the wastewater can sometimes be impossible without filtering the water which generally leads to a reduction in the biocide so ascertaining the true concentration in the fluid is difficult. The biocide demand of the fluid is also very high due to the amount of dissolved metals present. Therefore, biocides such as chlorine dioxide are generally mixed with fresh water at concentrations up to 20mg/l and dosed into the produced or flowback water. As with the fresh water treatment described in the previous page, an in-line amperometric probe method is used to control the dosing rate and a secondary method such as the Palintest ChlordioXense used to calibrate the probe and provide a secondary check method.

There is a growing trend within the water treatment industry to recover the hydrocarbons that are present in produced water and sell them onto the open market. The use of biocides such as chlorine dioxide helps increase the oil recovery rate as treatment causes the solids to precipitate out of solution and the hydrocarbons to settle on the top of the treated fluid.

Chlorine dioxide acts as a demulsifier to break up emulsions through chemical oxidation, allowing the water to separate from residual hydrocarbons, treatment chemicals and the particulate matter present.
The ‘clean’ water is usually of a good enough quality to be reused on another frack site or be disposed of via direct injection. The hydrocarbons can then be skimmed off and sold to oil companies, whilst the solid sludge is removed and transported to a standard wastewater facility.

An image of produced water (on the right) treated with chlorine dioxide (on the left).

Summary

The use of hydraulic fracturing as a process for increasing the yields of oil and gas wellbores is increasing, especially in the US, and its use will almost certainly spread to other countries.

Biocides are fundamental part of both the fracking fluid itself, and the treatment of the wastewater from the process.

Testing methods for quantifying biocide concentrations both in the freshwater and the wastewater have primarily been adopted from the drinking water industry where the water matrix is of a much ‘cleaner’ composition. Both colorimetric methods and ORP, although useful, do have their drawbacks and thus new methods such as the ChlordioXense are being readily adopted by the oil and gas industry.

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