PROCESS FOR HYDRAULIC FRACTURING WITH pH CONTROL

A process for hydraulic fracturing including the steps of (a) providing a fracturing fluid by combining water, proppant, an oxidizing biocide, and a friction reducer; (b) introducing the fracturing fluid into a well; and (c) controlling the pH of the fracturing fluid to a pH of at least about 4.5.
PROCESS FOR HYDRAULIC FRACTURING WITH PH CONTROL

FIELD OF THE INVENTION

[0001] The present invention relates to the stimulation of the production of subterranean hydrocarbon formations or stimulation of fluid injection into subterranean formations in a hydraulic fracturing process. More particularly, the present invention relates to an improved process for hydraulic fracturing in which performance of additives, in particular, friction reducers, is enhanced.

BACKGROUND OF THE INVENTION

[0002] The production of oil and natural gas from an underground well (subterranean formation) can be stimulated by a technique called hydraulic fracturing in which a fracturing fluid is introduced into an oil or gas well via a conduit, such as tubing or casing, at a flow rate and a pressure to create, reopen and/or extend a fracture into the well, allowing access to the oil or gas within the formation.

[0003] The fracturing fluid is typically a water based solution and may comprise components such as suspended propants (e.g., sand, bauxite); biocides to inhibit growth of bacteria and other microorganisms; corrosion inhibitors and scale inhibitors which reduce rust formation and other deposits on the conduit; and friction reducers to promote laminar flow of the hydraulic fracturing fluid into the formation and reduce the pumping pressure necessary to achieve the desired fracturing fluid flow rate.

[0004] Problems have been encountered in the performance of organic polymer friction reducers such as anionic polyacrylamide polymers (either hydrolyzed to produce acid functionality or copolymerized with acrylic acid). It has been theorized that use of oxidizing biocides in combination with these polymers causes the polymers to degrade and therefore increasing pumping pressure is necessary during the fracturing operations. Replacing an oxidizing biocide with a non-oxidizing biocide alleviates the problem of friction reducer performance. However, many non-oxidizing biocides are not acceptable due to environmental concerns and low efficacy. Non-oxidizing biocides include glutaraldehydes and quaternary amine-glutaraldehyde combinations.

[0005] In addition, friction reducing polymers can be sensitive to pH. It is known, for example, that performance of a hydrolyzed (anionic) polyacrylamide friction reducer is reduced at or below pH 4.5. At low pH, protonation of the polyacrylamide friction reducers can inhibit its ability to hydrate and unwind rapidly, thus, reducing its friction-reducing ability.

[0006] In hydraulic fracturing processes, after the fracturing fluid is introduced into the well, a substantial portion of the fracturing fluid is recovered, as the well is brought into production. The initial recovered fluid, referred to as “flow back water” contains contaminants such as hydrocarbons, minerals, and salts that are extracted from the formation during the fracturing process in addition to components of the fracturing fluid, including biocides, friction reducers, etc. that were introduced as part of the fracturing fluid. As production continues from the well, the water becomes “produced water”, which is the naturally occurring water in the formation. Flow back and produced water cannot simply be disposed of in a local stream, river, or shallow aquifer, but must be treated to remove contaminants. Because of the shortage of fresh water and the cost of treatment and/or disposal of produced water it is desirable to re-use at least a portion of the produced water in subsequent hydraulic fracturing treatments; however, the presence of contaminants, which include oxidizable, acid-producing metal ions, such as soluble Fe³⁺ and Mn²⁺, also negatively affects performance of the friction reducers. Once formed the Fe³⁺ and Mn²⁺ hydrolyze to produce Fe(OH)₃ and MnO₂ and acid.

[0007] It is highly desirable to avoid the need to increase pumping pressure to maintain fluid flow rate during hydraulic fracturing and to prevent performance issues related to contamination of or chemical reaction with friction reducers. It is desirable to use more acceptable biocides, which include oxidizing biocides, due to environmental concerns. It is desired to re-use at least a portion of produced water in a fracturing fluid, thus reducing the need for freshwater with each fracturing operation. These and other needs are satisfied by the present invention.

SUMMARY OF THE INVENTION

[0008] The present invention provides a process for hydraulic fracturing in which a fracturing fluid comprising a friction-reducing polymer and an oxidizing biocide is introduced into a well. The process comprises providing a fracturing fluid by (a) combining water, proppant, an oxidizing biocide, and a friction reducer; (b) introducing the fracturing fluid into a well; and (c) controlling the pH of the fracturing fluid to a pH of at least about 4.5. These process steps (a) through (c) can be performed in any suitable order.

[0009] Controlling pH surprisingly stabilizes performance of a friction reducer, when an oxidizing biocide is used. In addition, the process of this invention has a greater tolerance to contaminants from produced water.

[0010] In the process of this invention, pH may be controlled by: (i) measuring the pH of (1) at least one of the water, oxidizing biocide, or friction reducer, prior to step (a) or (2) the fracturing fluid, prior to or after the fracturing fluid is introduced into a well in step (b); (ii) comparing the measured pH with a set point of a desired pH; (iii) calculating the difference between the desired pH and the measured pH; and (iv) generating a signal which corresponds to the difference calculated in (iii) which provides a feedback response to a controller for adding a base to at least one of the water, oxidizing biocide or friction reducer or the fracturing fluid to control the pH of the fracturing fluid at a pH of at least about 4.5.

[0011] As an alternative to use of a feedback response, any one or all of the steps (i) through (iv) may be performed manually. For example, the pH of the desired component or fracturing fluid may be measured either manually or by an automated monitoring system. Comparing and calculating steps may be performed manually or electronically. The step of generating a signal may be an automated computer response to an in-line or on-line control system. Alternatively, individuals may monitor the pH and manually operate a feed pump to add base to the water, oxidizing biocide, or friction reducer, or the fracturing fluid. One operator may, for example, be positioned in a monitoring room observing pH, and may contact a second operator (i.e., generate and send a signal) with instructions (i.e., a feedback response) to add base, such as from a manual feed pump, to control pH.

[0012] It has been found that in the process of this invention, when pH of a fracturing fluid comprising a friction reducer and an oxidizing biocide is controlled at a pH of at
least about 4.5, performance issues previously encountered with deterioration of friction reducer performance, such as, increased pressure being required to sustain a desired flow rate, are substantially reduced. It has been further found that control of pH enables use of produced water blended into the hydraulic fracturing water without similar deleterious effects.

BRIEF SUMMARY OF THE FIGURE

FIG. 1 illustrates the providing of a fracturing fluid and the controlling of the pH thereof according to one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is a process for hydraulic fracturing wherein a fracturing fluid is introduced (injected) into an oil or gas well at a flow rate and a pressure to create, reopen and/or extend a fracture into the formation around the well, allowing access to the oil or gas within a subterranean formation.

The fracturing fluid comprises water, proppants, an oxidizing biocide and a friction reducer. The fracturing fluid may further comprise other components such as scale inhibitors and corrosion inhibitors. Surprisingly it has been found that performance of friction reducers does not deteriorate, that is, no undesirable pressure increases, in the presence of oxidizing biocides when pH of the fracturing fluid is controlled at a pH of at least about 4.5, preferably at least about 5.5. In general pH of the fracturing fluid is maintained at pH less than about 7.

By “oxidizing biocide” is meant herein a compound that has biocidal activity, meaning reduces the amount of bacteria and other microorganisms that may be present in the fracturing fluid as well as has the potential for oxidizing other components in the fracturing fluid. Examples of oxidizing biocides include bleach (sodium hypochlorite, NaOCl), peroxides, such as hydrogen peroxide, peracids, such as peroxyacetic acid, persulfates, ozone and chlorine dioxide. Preferred biocides include bleach, peracetic acid and chlorine dioxide.

The oxidizing biocide is generally added in an amount to provide a free residual in the fracturing fluid. The residual may be about 1-5 ppm of the oxidizing biocide. For example, about 50-90% of the biocide applied may be consumed. When the biocide is chlorine dioxide, for example, a dose of as great as 150 ppm ClO₂ may be required to provide a target of 1-5 ppm residual to achieve an appropriate level of disinfection.

Chlorine dioxide is a preferred oxidizing biocide. Chlorine dioxide is a gas and can be generated onsite at the oil or gas well location. Various methods are known for generating chlorine dioxide, including chemical and electrochemical processes as disclosed for example in Ullmann’s Encyclopedia of Industrial Chemistry, Wiley Online Library, http://onlinelibrary.wiley.com/doi/10.1002/14356007.a06 483, pub2/pdf, accessed Feb. 14, 2012. One particular method of generating chlorine dioxide involves reaction of an alkali metal chloride, such as sodium chloride with an acid, such as hydrochloric acid or sulfuric acid as illustrated below.

\[
5 \text{NaClO}_2 + 4\text{H}^+ \rightarrow 4\text{ClO}_2 + (g) + 2\text{H}_2\text{O} + 5\text{Na}^+
\]

If too much acid is used in generating chlorine dioxide, the generated product may have an undesirably low pH which can lower the pH of any fluid it is injected into. By controlling pH of the fracturing fluid as set forth herein, the issue of overfeeding acid from any source is addressed without adversely affecting performance of the friction reducer.

A friction reducer is added to a fracturing fluid to promote laminar flow of the fracturing fluid, which is important to achieve desired fracturing at lower pressures while maintaining high flow rates into the formation. Performance of the friction reducer is critical to achieve desired flow rates at desired pressure. Poor performance of a friction reducer causes increased pressure or reduced flow rate, either of which will negatively impact the fracturing process by increasing energy costs for higher pressure or increasing time and/or efficiency to achieve the desired fracturing at a lower pressure.

Friction reducers include organic polymers such as acrylic acid and acrylamide polymers and copolymers. Friction reducers may be anionic, cationic, and nonionic. Anionic friction reducers are lower cost and are the most widely used. Anionic friction reducers are typically modified polyacrylamide polymers (either hydrolyzed to produce acid functionality or copolymerized with acrylic acid) and have carboxylate functionalities. Anionic friction reducers having carboxylate functionality may be most susceptible to performance issues since these can be protonated at low pH values of 4.5 and below.

Fricction reducers may be an acrylic-acid-AMPS-polyacrylamide terpolymer, a brine dispersion AMPS-polyacrylamide copolymer, or a non-ionic polyacrylamide polymer. Friction reducers may be supplied as aqueous dispersions or mixed aqueous/petroleum distillate dispersions of a polymer concentrate. A preferred friction reducer is a polyacrylamide.

Friction reducers are typically dosed in an amount of 50-1000 ppm (parts per million by volume of polymer dispersion) based on the volume of the fracturing fluid.

In the hydraulic fracturing process large volumes of water are used. An advantage of the present invention is that when pH is suitably controlled, at least a portion of the water used for fracturing, which can average about 3000 gallons (11,000 liters) per minute, or more, can be flow back and produced water. Flow back water that is recovered from the fracturing operation and produced water may comprise metal salts including ferrous and ferrie metal salts, hydrocarbons, and residual biocide, friction reducer and other additives. In the absence of pH control as set forth herein, the presence of metal salts in the produced water interferes with performance of the friction reducer. In certain regions, such as in the Marcellus Shale region, produced water is characterized as having a high iron content.

Proppant, which keeps an induced hydraulic fracture open during or following a fracturing treatment, is most commonly sand but can also be any other such particulate material with adequate mechanical properties to withstand closure stresses including, for example, ceramic, glass, and bauxite.

The fracturing fluid may comprise other components, including, for example, polymers, breaking agents, scale inhibitors, corrosion inhibitors, etc. These other components may be added to the biocide or to the water, or still other options for adding are available.

The process of this invention comprises providing a fracturing fluid by combining water, proppant, an oxidizing biocide, and a friction reducer. This combining step may be in a single step or multiple steps.
For example, the water may be treated with the biocide and with other components such as a scale inhibitor and a corrosion inhibitor prior to combining the treated mixture with proppant and the friction reducer. The biocide treated water may be stored, for example for periods of time of about 30 minutes or less prior to combining with friction reducer. The water used may consist of all fresh water, usually from a local stream, pond, or potable water supply, or a mixture of fresh water and produced water. The fresh and produced water may be supplied to treatment manifold in a single stream or in multiple streams.

“Frac tanks” are often used as a source of water to supply a constant flow of water to the fracturing process. Water may be supplied to a blending/mixing device, such as a ribbon mixer into which friction reducer, proppant and biocide or biocide mixture are added to produce the fracturing fluid.

Once the fracturing fluid is produced, there is little time (maybe a matter of seconds) before the fracturing fluid is introduced into an oil or gas well. The fracturing fluid is introduced—or injected—into the well at a pressure of 2000-15,000 psi (13.8-103 MPa), typically 8000-10,000 psi (55-69 MPa). The flow rate is typically several thousand gallons per minute, such as 4000 gallons per minute (15,000 liters per minute).

In the process of this invention, pH of the fracturing fluid is controlled at a pH of at least about 4.5. Preferably pH is controlled at a pH of at least about 5.5. Generally pH is controlled at pH less than about 7, preferably less than about 6.5.

To control pH of the fracturing fluid, a measurement of pH is needed. This measurement may be taken of one or more of the components of the fracturing fluid, wherein the components of the fracturing fluid may be selected from the water, the biocide, or the friction reducer. Alternatively, the pH of the fracturing fluid may be measured. The pH of the fracturing fluid may be measured prior to or after introducing into the well. The measured pH is compared with a set point of a desired pH for the component or of the fracturing fluid. The difference between the desired pH and the measured pH is calculated. A signal is generated which corresponds to the calculated difference, which provides a feedback response to a controller for adding a base to at least one of the water, biocide or friction reducer or the fracturing fluid to control the pH of the fracturing fluid at a pH of at least about 4.5, preferably at least about 5.5.

The base can be an alkali metal salt or alkaline earth metal salt of hydroxide, oxide, bicarbonate, carbonate, or combinations of two or more thereof, as well as the base produced by ammonia dissolved into water (ammonium hydroxide base). Preferably the base is water soluble, more preferably the base is an aqueous solution.

In particular when produced water is used, it is preferred that the base will not cause precipitation of metal ions present in the produced water. If the produced water, for example, comprises barium, calcium and magnesium, the base is preferably an alkali metal hydroxide, more preferably an aqueous solution of ammonium hydroxide or an alkali metal hydroxide.

In general, preferred alkali metal hydroxide bases are hydroxides of lithium, sodium and potassium, more preferred as aqueous solutions. Most preferred are aqueous solutions of ammonium hydroxide, or sodium hydroxide, potassium hydroxide or a combination thereof.

FIG. 1 illustrates the providing of a fracturing fluid and the controlling of the pH of the fracturing fluid according to a process for hydraulic fracturing. Certain detailed features of the present process, such as pumps, flow controllers, feed tanks, and other ancillary equipment, are not shown for the sake of simplicity and in order to demonstrate the main features of the process. Such ancillary features can be easily designed and used by one skilled in the art without any difficulty or undue experimentation.

Referring to FIG. 1, water from feed line 12 is treated by contact with chlorine dioxide biocide from feed line 15 and delivered to reservoir 21 commonly referred to as a “frac tank”. The pH of the treated water is measured 18 and a suitable amount of base is injected via line 16 to control the pH to a value of at least greater than 4.5. The chlorine dioxide-treated water with pH greater than 4.5 is drawn from the frac tank through line 32 and contacted with friction reducer from line 34 and proppant from line 35 in mixing vessel 37 to form the finished fracturing fluid which is then introduced via line 38 to the well.

EXAMPLES

The identity of the commercial polymeric friction reducers used in these examples, all of which were obtained from Kemira (Kennesaw, Ga., USA), is as follows: KemFlow™ A4251 is an anionic, hydrolyzed polyacrylamide polymer; KemFlow™ A4358 is an anionic polyacrylamide acrylic acid copolymer; and KemFlow™ C4107 is a cationic polyacrylamide polymer.

Example 1

This example provides the results of friction loop tests which demonstrate the effect of pH on friction reduction of various friction reducing polymers.

Friction loop tests were carried out at Stim-Lab, Inc. located in Duncan, Okla., using a standard apparatus known to those skilled in the art. For each test, approximately 9 gallons of test fluid was circulated at 10 gallons/minute (approx. Reynolds number of 75,000). The friction reduction was calculated from the pressure drop across a precise length of the test loop.

The water used to prepare the test fluids was a blend of 40% produced water from the Marcellus shale formation and 60% surface water collected from a location in Pennsylvania. The unadjusted pH of the water was 5.8. For tests run at lower pH, the water was acidified with sulfuric acid. In some cases the acidified water was also treated to contain about 10 mg/L residual ClO₂. The test temperature was about 24°C (75°F).

For each test, a baseline differential pressure and flow rate was established for the fluid without friction reducer. The friction reducer was then injected into the test fluid at a rate of 500 parts per million (ppm) on a volume basis, and the percent friction reduction compared to baseline was determined. Results were recorded after 5, 10 and 14 minutes of continuous operation, and are shown in Table 1. Tests on each of the friction reducers were run under varying conditions of solution pH and residual ClO₂ concentration as indicated in tests 1A-H in the table below.
It can be seen that the lower pH has a substantial
negative effect on the friction reduction ability of the anionic
copolymer A4251 and A4358. Thus, the friction reduc-
tion of A4251 at pH 3.4 (1B) is much less than the friction
reduction of the same material at pH 5.8 (1A). Likewise, the
friction reduction of A4358 at pH 3.5 (1E) is much less than
the friction reduction of the same material at pH 5.8 (1D).
The friction reduction ability of the cationic polycryl
amides such as C4107 (1F and 1G) is substantially unaffected
by pH changes in the range of 3.5 to 5.8. Test fluids 1C and 1H
illustrate that adjustment of pH upward with a source of
alkali, such as sodium bicarbonate (NaHCO3), after ClO2
treatment, resulted in the preservation of acceptable friction
reduction performance.

Example 2

This example demonstrates the pH lowering effect
of oxidizing biocide in combination with divalent iron.

Unbuffered deionized water was adjusted to a pH of
6.0-6.2 with 1N NaOH or HCl as needed. Samples 2B and 2C
were prepared from this water and 99.5% iron(II) hepta-
hydrate so that the added Fe2+ content was 25 and 50 mg/L,
respectively. Sample 2A was a control sample and contained
no added iron. To each of samples 2A-2C, 30 mg/L ClO2 was
applied, after which the pH and residual ClO2 was measured
about 30 minutes later. Results, which were gathered at ambient
laboratory temperatures of about 20-22 C, are summa-
rized in the following table.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe2+ mg/L</th>
<th>pH initial</th>
<th>pH final</th>
<th>ClO2 mg/L</th>
<th>ClO22 mg/L</th>
<th>ClO2 residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>2A</td>
<td>0</td>
<td>6.18</td>
<td>6.24</td>
<td>30</td>
<td>18.1</td>
<td>11.3</td>
</tr>
<tr>
<td>2B</td>
<td>25</td>
<td>6.10</td>
<td>3.61</td>
<td>30</td>
<td>14.5</td>
<td></td>
</tr>
<tr>
<td>2C</td>
<td>50</td>
<td>6.10</td>
<td>3.3</td>
<td>30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Control sample 2A, without Fe2+, shows no sub-
stantial change in pH with addition of ClO2 and substantially
no consumption of ClO2. The applied and residual amount is
substantially the same. In contrast, ClO2 addition to Fe2+-
containing samples 2B and 2C causes substantial decrease in
pH to levels below 4.5. Consistent with the oxidation of the
iron, the residual ClO2 level in 2B and 2C is lower than control
sample 2A.

From these results, it can be appreciated that rela-
tively neutral pH water taken from the environment, compris-
ing common minerals such as iron, can be reduced in pH
below 4.5 when treated with oxidizing biocides such as chlori-
ne dioxide.

What is claimed is:

1. A process for hydraulic fracturing comprising
   (a) providing a fracturing fluid by combining water, prop-
   pellant, an oxidizing biocide, and a friction reducer;
   (b) introducing the fracturing fluid into a well; and
   (c) controlling the pH of the fracturing fluid to a pH of at
   least about 4.5.

2. The process of claim 1 wherein the pH is controlled by (i)
   measuring the pH of (1) at least one of the water, oxidizing
   biocide, or friction reducer, prior to combining step (a) or (2)
   the fracturing fluid, prior to or after the fracturing fluid is
   introduced into a well in step (b); (ii) comparing the measured
   pH with a set point of a desired pH; (iii) calculating the
difference between the desired pH and the measured pH; and
   (iv) generating a signal which corresponds to the difference
calculated in (iii) which provides a feedback response to a
controller for adding a base to at least one of the water,
biocide or friction reducer or the fracturing fluid to control
the pH of the fracturing fluid at a pH of at least about 4.5.

3. The process of claim 3 wherein any one or all of the steps
   (i) through (iv) is performed manually.

4. The process of claim 3 wherein the base is ammonium
   hydroxide, an alkali metal salt or alkaline earth metal salt of
   hydroxide, oxide, bicarbonate, carbonate, or combinations of
two or more thereof.

5. The process of claim 1 wherein the oxidizing biocide is
   selected from the group consisting of bleach, peroxides, per-
   acids, persulfates, ozone, chlorine dioxide, and combinations
   thereof.

6. The process of claim 1 wherein the friction reducer is an
   anionic polyacrylamide or polyacrylamide co-polymer.

7. The process of claim 1 wherein the pH is at least about
   5.5.

8. The process of claim 1 wherein the pH is less than about
   pH 7.

9. The process of claim 2 wherein the pH of the fracturing
   fluid is measured and is measured prior to introducing the
   fracturing fluid into the well.

10. The process of claim 2 wherein at least a portion of the
    water is produced water.

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