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(54) **Title**: PROCESS FOR TREATING AND RECYCLING HYDRAULIC FRACTURING FLUID

(57) **Abstract**: A novel method for treating hydraulic fracturing fluid is disclosed. The hydraulic fracturing fluid is treated with an anionic silica-based colloid in an amount and for a sufficient time to coagulate certain contaminants contained in the hydraulic fracturing fluid. The contaminants can thereafter be removed from the hydraulic fracturing fluid.

# PROCESS FOR TREATING AND RECYCLING HYDRAULIC FRACTURING FLUID

## FIELD OF THE INVENTION

The present invention relates to an improved process for removing certain contaminants from hydraulic fracturing fluids. The treated fracturing fluids can be recycled and used in subsequent hydraulic fracturing processes.

## BACKGROUND OF THE INVENTION

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.

The fracturing fluid is typically a water based solution and may comprise components such as suspended proppants (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.

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. Recycled produced and flow back fluids are increasingly used as source waters for hydraulic fracturing operations. Such water sources are complex in nature in that they are rich in soluble and insoluble inorganic salts and organic compounds. The presence of oxidizable metal ion salts, such as $Fe^{2+}$ and $Mn^{2+}$ salts, pose a unique challenge when oxidized by air or by oxidizing biocides, the latter used to disinfect the water. Aerial oxidation is a relatively slow process, but oxidizing biocides rapidly and quantitatively oxidize $Fe^{2+}$ to $Fe^{3+}$ and $Mn^{2+}$ to $Mn^{4+}$ with the concomitant precipitation of colloidal $Fe(OH)_3$ and $MnO_2$, respectively, at or near neutral pH. $Fe^{2+}$ is generally more abundant than $Mn^{2+}$, therefore precipitation of $Fe(OH)_3$ is potentially more of a problem than $MnO_2$. If untreated, colloidal $Fe(OH)_3$, in high-enough concentration, can interfere with hydraulic fracturing operations (e.g., due to complexing and flocculation of friction reducing polymers,). This will result in undesirably low hydraulic flow rates and undesirably high pumping pressure. This in turn will result in incomplete fracturing of the formation and limits the amount of gas or oil production over time. One approach to address this problem is by conventional filtration of the precipitated colloidal $Fe(OH)_3$. However, if iron loading is too high, filtration can be very costly and labor intensive due to frequent blinding and changing of filter media. Thus, the art would benefit from an improved, robust process for providing recycled fracturing fluid. The present invention provides such a process.

## BRIEF SUMMARY OF THE INVENTION

The present invention provides a method for reducing the concentration of soluble and suspended oxidizable metal ion salts in an aqueous, hydraulic fracturing source fluid comprising the steps of: providing an aqueous, hydraulic fracturing source fluid containing oxidizable metal ion salts; oxidizing at least some of the oxidizable metal ion salts; contacting the aqueous, hydraulic fracturing source fluid with an anionic silica-based colloid for a time sufficient to coagulate at least a portion of the suspended oxidized metal ion salts; and separating the oxidized metal ion salts from the hydraulic fracturing source fluid.

In one aspect of the invention the step of oxidizing at least some of the oxidizable metal ion salts is achieved by aerial oxidation. In a preferred aspect of the invention the step of oxidizing at least some of the oxidizable metal ion salts is achieved by treating the aqueous, hydraulic fracturing source fluid with an oxidizing biocide.

In an aspect of the invention it may be desirable to adjust the pH of the source fluid. The pH can be adjusted either before or after contacting the source fluid with the anionic silica-based colloid. It may be desirable to control the pH in the range of about 5.0 to about 8.0. It may be even more desirable to control the pH in the range of about 6.0 to about 7.0. The pH can be achieved by any suitable means as one skilled in the art will understand. For example, a suitable base, such as sodium hydroxide or ammonium hydroxide can be used to control the pH in the above ranges.

In a further aspect of the invention the present invention provides a method for reducing the concentration of soluble and suspended oxidizable metal ion salts in an aqueous, hydraulic fracturing source fluid consisting essentially of the following steps: providing an aqueous, hydraulic fracturing source fluid containing oxidizable metal ion salts; treating the aqueous, hydraulic fracturing source fluid with an oxidizing biocide to oxidize at least some of the oxidizable metal ion salts; contacting the treated fluid with an anionic silica-based colloid for a time sufficient to coagulate at least a portion of the suspended metal ion salts;

and separating the oxidized metal ion salts from the hydraulic fracturing source fluid.

In an aspect of the invention the oxidizing biocide can comprise a material selected from the group consisting of chlorine bleach, peroxides, peracids, persulfates, ozone, chlorine dioxide, and combinations thereof. In a particular aspect the oxidizing biocide can comprise chlorine dioxide.

In a further aspect of the invention the anionic silica-based colloid can comprise a material selected from the group consisting of polysilicic acid, polysilicic acid microgels, polysilicate microgels, polyaluminosilicate microgels, colloidal silicas and combinations thereof.

The oxidizable metal ion can comprise a material selected from the group consisting of ferrous ion and manganous ion. In one aspect the oxidizable metal ion comprises ferrous ion.

In an aspect of the invention the aqueous, hydraulic fracturing source fluid can further comprise at least one material selected from the group consisting of alkali metal salts, alkaline-earth metal salts, friction reducing polymer, scale inhibitor, corrosion inhibitor, hydrocarbon and proppant.

In a further aspect of the invention, the method may further include the step of adding a cationic organic polymer to the hydraulic fracturing source fluid.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a method for reducing the concentration of soluble and suspended oxidizable metal ion salts in an aqueous, hydraulic fracturing source fluid comprising the steps of: providing an aqueous, hydraulic fracturing source fluid containing oxidizable metal ion salts; oxidizing at least some of the oxidizable metal ion salts; contacting the aqueous, hydraulic fracturing source fluid with an anionic silica-based colloid for a time sufficient to coagulate at least a portion of the suspended oxidized metal ion salts; and separating the oxidized metal ion salts from the hydraulic fracturing source fluid.

In one aspect of the invention the step of oxidizing at least some of the oxidizable metal ion salts is achieved by aerial oxidation. In a preferred aspect of the invention the step of oxidizing at least some of the oxidizable metal ion salts is achieved by treating the aqueous, hydraulic fracturing source fluid with an oxidizing biocide.

In an aspect of the invention it may be desirable to adjust the pH of the source fluid. The pH can be adjusted either before or after contacting the source fluid with the anionic silica-based colloid. It may be desirable to control the pH in the range of about 5.0 to about 8.0. It may be even more desirable to control the pH in the range of about 6.0 to about 7.0. The pH can be achieved by any suitable means as one skilled in the art will understand. For example, a suitable base, such as sodium hydroxide or ammonium hydroxide can be used to control the pH in the above ranges.

In a further aspect of the invention the present invention provides a method for reducing the concentration of soluble and suspended oxidizable metal ion salts in an aqueous, hydraulic fracturing source fluid consisting essentially of the following steps: providing an aqueous, hydraulic fracturing source fluid containing oxidizable metal ion salts; treating the aqueous, hydraulic fracturing source fluid with an oxidizing biocide to oxidize at least some of the oxidizable metal ion salts; contacting the treated fluid with an anionic silica-based colloid for a time sufficient to coagulate at least a portion of the suspended metal ion salts; and separating the oxidized metal ion salts from the hydraulic fracturing source fluid.

In an aspect of the invention at least a portion of the suspended metal ion salts are allowed to settle before the salts are separated from the hydraulic fluid.

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 to oxidize other components in the fracturing fluid. Examples of oxidizing biocides include chlorine bleach (sodium hypochlorite, NaOCl), peroxides, such as hydrogen peroxide, peracids, such as

peracetic acid, persulfates, ozone, chlorine dioxide, and combinations thereof. Preferred biocides include chlorine 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 $ClO_2$ 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 February 14, 2012. One particular method of generating chlorine dioxide involves reaction in aqueous solution of an alkali metal chlorite salt, such as sodium chlorite, with sodium hypochlorite and a source of strong acid as illustrated below.

$$2NaClO_2 + NaOCl + 2HCl \rightarrow 2ClO_2 + 3NaCl + H2O$$

Although any suitable colloidal silica may be useful according to the invention, in a further aspect of the invention the anionic silica-based colloids may have an S value of less than about 50%, as defined in Iler and Dalton in *J. Phys. Chem.*, 1956, vol. 60, pp. 955-957. The S value is a measure of the degree of aggregate or microgel formation and a lower S value indicates a higher microgel content and is determined by the measure of the amount of silica, in weight percent, in the disperse phase. The disperse phase consists of particles of anhydrous silica together with

any water that is immobilized at the surface or in the interior of the particles.

Examples of anionic silica-based colloids which can be used in the process of this invention include colloidal silica, polysilicic acid, polysilicic acid microgels, polysilicate microgels, polyaluminosilicate microgels, colloidal silicas with a high microgel content, and mixtures thereof. Preferably the anionic silica-based colloids have an S value of less than about 50% and preferably less than 40%.

Polysilicate microgels, also known as active silicas, have $SiO_2$:$Na_2O$ ratios of 4:1 to about 25:1, and are discussed on pages 174-176 and 225-234 of "The Chemistry of Silica" by Ralph K. Iler, published by John Wiley and Sons, N. Y., 1979. Polysilicic acid generally refers to those silicic acids that have been formed and partially polymerized in the pH range 1-4 and comprise silica particles generally smaller than 4 nm diameter, which thereafter polymerize into chains and three-dimensional networks. Polysilicic acid can be prepared, for example, in accordance with the methods disclosed in U. S. Patent 5,127,994, incorporated herein by reference.

Polyaluminosilicates are polysilicate or polysilicic acid microgels in which aluminum has been incorporated within the particles, on the surface of the particles, or both.

The polysilicate microgels and polyaluminosilicate microgels useful in this invention are commonly formed by the activation of an alkali metal silicate under conditions described in U. S. Patents 4,954,220 and 4,927,498, incorporated herein by reference. However, other methods can also be employed. For example, polyaluminosilicates can be formed by the acidification of silicate with mineral acids containing dissolved aluminum salts as described in U. S. Patent 5,482,693, incorporated herein by reference. Alumina/silica microgels can be formed by the acidification of silicate with an excess of alum, as described in U. S. Patent 2,234,285, incorporated herein by reference.

The anionic silica-based colloid can be provided in any suitable amount. In an aspect of the invention the anionic silica-based colloid can be provided in an amount from about 0.1 to about 1000 ppm, and more preferably in an amount from about 1.0 to about 1000 ppm, based on the $SiO_2$ content. The oxidizable metal ion can comprise a material selected from the group consisting of ferrous ion and manganous ion. In one aspect the oxidizable metal ion comprises ferrous ion.

In a further aspect of the invention, the method may further include the step of adding a cationic organic polymer to the hydraulic fracturing source fluid. In an aspect of the invention, the cationic organic polymer may be added after the anionic silica-based colloid. High molecular weight and low molecular weight polymers may be used. The cationic organic polymer can be provided in any suitable amount. In an aspect of the invention the cationic organic polymer can be provided in an amount from about 0.5 to about 1000 mg of polymer per liter of aqueous fluid, and preferably in an amount from about 1 to about 100 mg per liter of aqueous fluid.

High molecular weight cationic organic polymers include natural and synthetic cationic polymers. Natural cationic polymers include cationic starch, cationic guar gum, and chitosan. High molecular weight synthetic cationic polymers typically have number average molecular weights greater than 1,000,000, such as cationic polyacrylamide. Cationic starches include those formed by reacting starch with a tertiary or quaternary amine to provide cationic products with a degree of substitution of from 0.01 to 1.0, containing from about 0.01 to 1.0 wt. % nitrogen. Suitable starches include potato, corn, waxy maize, wheat, rice and oat. Preferably the high molecular weight cationic organic polymer is polyacrylamide.

Low molecular weight cationic organic polymers have a number average molecular weight in the range between about 2,000 to about 1,000,000, preferably between 10,000 and 500,000. The low molecular weight polymer can be polyethylene imine, polyamines, polycyandiamide formaldehyde polymers, amphoteric polymers, diallyl dimethyl ammonium

chloride polymers, diallylaminoalkyl (meth)acrylate polymers and dialkylaminoalkyl (meth)acrylamide polymers, a copolymer of acrylamide and diallyl dimethyl ammonium chloride, a copolymer of acrylamide and diallylaminoalkyl (meth)acrylates, a copolymer of acrylamide and dialkyldiaminoalkyl (meth)acrylamides, and a polymer of dimethylamine and epichlorohydrin. These have been described in U.S. Pat. Nos. 4,795,531 and 5,126,014.

In an aspect of the invention the aqueous, hydraulic fracturing source fluid can further comprise at least one material selected from the group consisting of alkali metal salts, alkaline-earth metal salts, friction reducing polymer, scale inhibitor, corrosion inhibitor, hydrocarbon, and proppant.

A friction reducer can be added to the 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 pump 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.

Suitable friction reducers can 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.

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.

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.

## ANALYTICAL METHODS

The following analytical methods and instrumentation were used in the examples to follow.

Approximately 3000 mg/L stock solutions of chlorine dioxide were prepared by stoichiometric reaction of aqueous 9 weight percent sodium chlorite and 8.2 weight percent sodium hypochlorite and acidified to about pH 3 with 1N hydrochloric acid in accordance with DuPont Method ANOG-402, "Preparation of Chlorine Dioxide Stock Solutions by Mass". Analysis of the stock solution was carried out using DuPont Method ANOG-404, adapted from Standard Method 4500-$ClO_2$ E, "Standard Methods for the Examination of Water and Wastewater", 20$^{th}$ edition, 1998.

One weight percent (SiO2 basis) solutions of polysilicic acid microgel were prepared according to methods described in US 6,203,711 B1.

Turbidity: At each indicated time point, a 25 mL sample of the supernatant was withdrawn from the reaction vessel by pipette and reserved for analysis. At the conclusion of each experiment, each sample was well-mixed, transferred to a sample cell, and the turbidity was measured using a Hach Model 2100N turbidimeter (Hach Company, Loveland, CO). Results are reported in Nephelometric turbidity units (NTU).

Total iron analysis was carried out on the same sample used for turbidity measurements by one of two methods as indicated in the examples:

(1) Inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin Elmer Optimum 5300 radial view instrument. Samples were well-mixed and digested in 10% nitric acid prior to analysis. Results are reported in units of mg/kg.

(2) Ferrover® total iron method using a Hach DR900 portable colorimeter (Hach Company, Loveland CO). Samples were diluted 1:100 by volume in deionized water prior to analysis and the results were reported in units of mg/L.

pH and ORP (oxidation-reduction potential) measurements were made using an Orion™ Dual Star™ pH/ISE Meter (Thermo Scientific Co., www.thermoscientific.com). pH was measured using an Orion™ 9107BN Triode™ 3-in-1 pH/Automatic Temperature Compensation probe (9107BNMD). OrP was measured using an Orion™ Combination Redox/ORP electrode (#9678BNWP).

## EXAMPLES

**Example 1**

Produced water from the Marcellus region was obtained and characterized as follows:

| | |
|---|---|
| pH 6.0 | TOC 181 mg/L |
| Ba 140 mg/kg | Ca 19,200 mg/kg |
| Fe 48 mg/kg | K 8170 mg/kg |
| Mg 1600 mg/kg | Mn 6 mg/kg |
| Na 74,700 mg/kg | Sr 2400 mg/kg |

A dose of 30 mg/L of chlorine dioxide (using a 3500 mg/L aqueous stock solution) was added to a 100-mL sample of the produced water in a 150-mL beaker, with stirring at 50 rpm, in order to satisfy the oxidative and microbial demand of the aqueous fluid. The chlorine dioxide was allowed to react for about five minutes, after which time the pH and oxidation-reduction potential (ORP) of the solution were measured and found to be 4.38 and >900 mV, respectively. A dose of 10 mg/L ($SiO_2$ basis) of a 1.0 wt.% ($SiO_2$ basis) solution of polysilicic acid microgel of the present invention was then added and the stir rate was increased to 200 rpm. The pH was adjusted dropwise to 6.98 with aqueous ammonia (28-30 wt.%). At this point the stirrer was turned off and the rust-colored coagulum that had formed was allowed to settle. The settling time was measured and found to be about 61 seconds. Settling time was determined by visual inspection when nearly (>95%) complete.

**Example 2**

Another 100-mL sample of produced water was treated with chlorine dioxide as described in Example 1. In this case, a dose of 100 mg/L ($SiO_2$ basis) of a 1.0 wt.% ($SiO_2$ basis) solution of polysilicic acid microgel was used. The pH was adjusted from 3.91 to 6.71 with aqueous ammonia. When the stirrer was turned off, the rust-colored coagulum was found to settle in about 17 seconds, even more rapidly than in Example 1.

**Comparative Example A**

Another 100-mL sample of produced water was treated with chlorine dioxide as described in Example 1. In this case, no polysilicic acid microgel was added. The pH was adjusted from 4.17 to 6.88 with aqueous ammonia. When the stirrer was turned off, the rust-colored coagulum was found to settle in about 138 seconds, more slowly than in Examples 1 and 2.

For Comparative Example B and Examples 3-6, another produced water from the Marcellus region was obtained and characterized as follows:

| | |
|---|---|
| pH 4.5 | |
| Ba 183 mg/kg | Ca 14,500 mg/kg |
| Fe 201 mg/kg | K 953 mg/kg |
| Mg 1620 mg/kg | Mn 14 mg/kg |
| Na 40,300 mg/kg | Sr 2930 mg/kg |

**Comparative Example B**

A 200-mL sample of the produced water described above was treated with 20 mg/L chlorine dioxide (using a 2420 mg/L aqueous stock solution) in a 250-mL beaker, with stirring at 50 rpm. The chlorine dioxide was allowed to react for about five minutes, after which time the pH and oxidation-reduction potential (ORP) of the solution were measured and found to be 3.17 and >900 mV, respectively. As in Comparative Example A, no polysilicic acid microgel was added. The stir rate was increased to 200 rpm and the pH was adjusted dropwise with aqueous ammonia (28-30 wt.%) from 3.17 to 6.31. At this point the stirrer was turned off (time = 0) and the rust-colored coagulum began to settle. Samples of the supernatant were taken for turbidity measurements and total iron analysis at time = 15, 30 and 60 seconds. These data are provided in Table 1. The total time for complete settling was about 146 seconds.

**Example 3**

Another 200-mL sample of produced water was treated with chlorine dioxide as described in Comparative Example B. A dose of 5 mg/L ($SiO_2$ basis) of a 1.0 wt.% ($SiO_2$ basis) solution of polysilicic acid microgel was then added and the stir rate was increased to 200 rpm. The pH was adjusted dropwise with aqueous ammonia from 3.18 to 6.20. The stirrer

was then turned off and the rust-colored coagulum was allowed to settle. Samples of the supernatant were taken as described in Comparative Example B for turbidity measurement and total iron analysis at t= 15, 30 and 60 seconds (Table 1). The total time for complete solids settling was about 106 seconds. The data show that, at each time point, the turbidity and iron content of the supernatant are reduced in this example due to the addition of an anionic silica-based colloidal microgel versus that in Comparative Example B. Likewise, the overall time for complete solids settling was reduced versus Comparative Example B.

**Example 4**

As described in Example 3, another 200-mL sample of produced water was treated with chlorine dioxide and 5 mg/L (SiO2 basis) of polysilicic acid microgel. The stir rate was increased from 50 to 200 rpm and the pH was adjusted dropwise with aqueous ammonia from 3.18 to 6.47. At this point 50 mg/L Zetag® 8818 cationic polyacrylamide polymer solution (BASF Corporation North America, Florham Park, NJ; 40% active) was added using a 1/400 aqueous dilution of the product. The sample was allowed to stir until a flocculated solid suspension was fully-formed (about 1-2 minutes). At this point the stirrer was turned off and the solids were allowed to settle. Samples of the supernatant were taken as described in Comparative Example B for turbidity measurement and total iron analysis at t= 15, 30 and 60 seconds (Table 1). The total time for complete solids settling was about 54 seconds. It can be seen from the data that overall settling time, and supernatant turbidity and total iron content at all time points are further reduced with the sequential addition of an anionic silica-based colloidal microgel and a cationic organic polymer.

**Example 5**

This example illustrates the use of a cationic polyacrylamide friction reduction polymer in combination with an anionic silica-based colloid to accelerate solids settling in a produced water sample.

As described in Example 4, another 200-mL sample of produced water was treated with chlorine dioxide and 5 mg/L (SiO2 basis) of polysilicic acid microgel. The stir rate was increased from 50 to 200 rpm and the pH was adjusted dropwise with aqueous ammonia from 3.17 to 6.38. At this point 50 mg/L KemFlow™ C4107 cationic polyacrylamide polymer solution (Kemira Chemicals, Inc., Atlanta, GA; 10-30% active) was added using a 1/1000 aqueous dilution of the product. The sample was allowed to stir until a flocculated solid suspension was fully-formed (about 1-2 minutes). At this point the stirrer was turned off and the solids were allowed to settle. Samples of the supernatant were taken as described in Comparative Example B for turbidity measurement and total iron analysis at t= 15, 30 and 60 seconds (Table 1). The total time for complete solids settling was 48 seconds. As in Example 4, it can be seen from the data that overall settling time and supernatant turbidity and total iron content at all time points are further reduced with the sequential addition of the anionic silica-based colloidal microgel and a cationic friction reduction polymer.

**Example 6**

This example illustrates the utility of a lower dose of cationic organic polymer in combination with an anionic silica-based colloidal microgel.

As described in Example 4, another 200-mL sample of produced water was treated with chlorine dioxide and 5 mg/L (SiO2 basis) of polysilicic acid microgel. The stir rate was increased from 50 to 200 rpm and the pH was adjusted dropwise with aqueous ammonia from 3.17 to 6.41. At this point 12.5 mg/L Zetag® 8818 cationic polyacrylamide polymer solution was added using a 1/400 aqueous dilution of the product. The sample was allowed to stir until a flocculated solid suspension was fully-formed (about 1-2 minutes). At this point the stirrer was turned off and the solids were allowed to settle. Samples of the supernatant were taken as described in Comparative Example B for turbidity measurement and total iron analysis at t= 15, 30 and 60 seconds (Table 1). The total time for complete solids settling was 50 seconds. It can be seen from the data that in all aspects a

lower dose of polymer is nearly as effective as the higher dose used in Example 4.

A synthetic brine solution (used to closely replicate a produced water sample) with the following composition was prepared in deionized water for use in Examples 7 and 8, and Comparative Examples C - F.

64.4 g/kg CaCl2.2H2O (20,000 mg/kg Ca2+)

127.1 g/kg NaCl (50,000 mg/kg Na+)

5.86 g/kg MgCl2 (1500 mg/kg Mg2+

**Example 7**

About 99.6 mg of ferrous sulfate heptahydrate, $FeSO_4.7H_2O$ was dissolved in 200 mL of synthetic brine solution (100 mg/L as $Fe^{2+}$ ) and was treated with 35 mg/L chlorine dioxide (using a 2380 mg/L aqueous stock solution) ) and 10 mg/L (SiO2 basis) of polysilicic acid microgel as described in Example 1. The stir rate was increased from 50 to 200 rpm and the pH was adjusted dropwise with aqueous ammonia from 2.93 to 6.39. The sample was allowed to stir until a coagulated solid suspension was fully-formed (about 1-2 minutes). At this point the stirrer was turned off and the solids were allowed to settle. Samples of the supernatant were taken as described in Comparative Example B for turbidity measurement and total iron analysis at t= 15, 30 and 60 seconds (Table 2). The total time for complete solids settling was 97 seconds.

**Example 8**

Another 200 mL sample of synthetic brine solution was prepared as described in Example 7, treated with 35 mg/L chlorine dioxide and 10 mg/L (SiO2 basis) of polysilicic acid microgel. The stir rate was increased from 50 to 200 rpm and the pH was adjusted dropwise with aqueous

ammonia from 2.91 to 6.65. At this point 50 mg/L Zetag® 8818 cationic polyacrylamide polymer solution was added using a 1/400 aqueous dilution of the product. The sample was allowed to stir until a flocculated solid suspension was fully-formed (about 1-2 minutes). At this point the stirrer was turned off and the solids were allowed to settle. Samples of the supernatant were taken as described in Comparative Example B for turbidity measurement and total iron analysis at t= 15, 30 and 60 seconds (Table 2). The total time for complete solids settling was 58 seconds. As in Examples 4-6, more rapid reduction in supernatant turbidity and iron content is observed, along with a concomitant reduction in settling time, with the sequential addition of an anionic silica-based colloidal microgel and a cationic organic polymer.

**Comparative Example C**

Another sample of synthetic brine solution was prepared and treated with chlorine dioxide as described in Example 7. In this case, no polysilicic acid microgel or cationic organic polymer was added. The pH was adjusted from 2.90 to 6.48 with aqueous ammonia. At this point the stirrer was turned off and the solids were allowed to settle. Samples of the supernatant were taken as described in Comparative Example B for turbidity measurement and total iron analysis at t= 15, 30 and 60 seconds (Table 2). The total time for complete solids settling was 160 seconds. As observed in Comparative Example B, the data show that, overall settling time, and supernatant turbidity and iron content at each time point are reduced less rapidly than in Examples 7 and 8.

Comparative Examples D and E show that without the addition of chlorine dioxide, reduction in the concentration of soluble and suspended oxidizable metal ion salts (e.g., iron salts) is not achieved.

**Comparative Example D**

Another 200 mL sample of synthetic brine solution was prepared as described in Example 7, but was not treated with chlorine dioxide. However, it was treated with 10 mg/L ($SiO_2$ basis) of polysilicic acid microgel solution. The resultant pH after microgel addition was 6.33, so no further pH adjustment was required. Supernatant turbidity and iron concentration measurements were made as described in Comparative Example B (Table 2). A settling time was not determined as there were no visible suspended solids present.

**Comparative Example E**

Another 200 mL sample of synthetic brine solution was prepared as described in Comparative Example D without chlorine dioxide treatment. In this case it was treated with 10 mg/L ($SiO_2$ basis) of polysilicic acid microgel solution and 50 mg/L Zetag® 8818 cationic polyacrylamide polymer solution as described in Example 8. The resultant pH after polmer addition was 6.14, so no further pH adjustment was required. Supernatant turbidity and iron concentration measurements were made as described in Comparative Example B (Table 2). The total time for complete solids settling was 110 seconds.

**Comparative Example F**

Another 200 mL sample of synthetic brine solution was prepared and treated with 35 mg/L chlorine dioxide as described in Example 7. In this case, no polysilicic acid microgel solution was added. The pH was adjusted from 2.91 to 6.52 with aqueous ammonia and 50 mg/L Zetag® 8818 cationic polyacrylamide polymer solution was added as described in Example 8. At this point the stirrer was turned off and the solids were allowed to settle. Samples of the supernatant were taken as described in Comparative Example B for turbidity measurement and total iron analysis at t= 15, 30 and 60 seconds (Table 2). The total time for complete solids settling was 84 seconds. The data show that, post $ClO_2$ oxidation, the addition of only a cationic organic polymer is not as effective at reducing the concentration of soluble and insoluble iron salts versus the sequential

addition of an anionic silica-based colloidal microgel and a cationic organic polymer.

## TABLE 1

| | Comp. Exp. B | | Exp. 3 | | Exp. 4 | | Exp. 5 | | Exp. 6 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sampling time (sec) | Turbidity (NTU)[1] | Total Iron (mg/kg)[2] | Turbidity (NTU) | Total Iron (mg/kg) | Turbidity (NTU) | Total Iron (mg/kg) | Turbidity (NTU) | Total Iron (mg/kg) | Turbidity (NTU) | Total Iron (mg/kg) |
| 15 | 828 | 166 | 406 | 92 | 23 | 27 | 29 | 31 | 29 | 36 |
| 30 | 213 | 67 | 151 | 59 | 15 | 27 | 19 | 30 | 19 | 32 |
| 60 | 120 | 50 | 74 | 43 | 14 | 26 | 17 | 29 | 15 | 31 |

## TABLE 2

| | Exp. 7 | | Exp. 8 | | Comp. Exp. C | |
|---|---|---|---|---|---|---|
| Sampling time (sec) | Turbidity (NTU) | Total Iron (mg/L)[3] | Turbidity (NTU) | Total Iron (mg/L) | Turbidity (NTU) | Total Iron (mg/L) |
| 15 | 66 | 91 | 28 | 24 | 69 | 94 |
| 30 | 48 | 65 | 7.7 | 7.4 | 65 | 86 |
| 60 | 23 | 29 | 5.8 | 3.9 | 46 | 58 |
| | Comp. Exp. D | | Comp. Exp. E | | Comp. Exp. F | |
| | Turbidity (NTU) | Total Iron (mg/L) | Turbidity (NTU) | Total Iron (mg/L) | Turbidity (NTU) | Total Iron (mg/L) |
| 15 | 12 | 99 | 23 | 82 | 55 | 62 |
| 30 | 12 | 100 | 22 | 78 | 28 | 24 |
| 60 | 12 | 100 | 18 | 79 | 14 | 12 |

1 Measured using a Hach 2100N turbidimeter (Hach Company).

2 Measured by inductively coupled plasma optical emission spectroscopy (ICP-OES).

3 Measured by FerroVer® total iron method using a Hach DR900 portable colorimeter(Hach Company).

## CLAIMS

What is claimed is:

1. A method for reducing the concentration of soluble and suspended oxidizable metal ion salts in an aqueous, hydraulic fracturing source fluid comprising the steps of:
    a. providing an aqueous, hydraulic fracturing source fluid containing oxidizable metal ion salts;
    b. oxidizing at least some of the oxidizable metal ion salts;
    c. contacting the aqueous, hydraulic fracturing source fluid with an anionic silica-based colloid for a time sufficient to coagulate at least a portion of the suspended metal ion salts; and
    d. separating the oxidized metal ion salts from the hydraulic fracturing source fluid.
2. The method of claim 1, further comprising the step of contacting the aqueous, hydraulic fracturing source fluid with a cationic organic polymer prior to step d.
3. The method of claim 1, wherein the at least some oxidizable metal ion salts are oxidized by aerial oxidation.
4. The method of claim 1, wherein the at least some oxidizable metal ion salts are oxidized by treating the aqueous, hydraulic fracturing source fluid with an oxidizing biocide.
5. The method of claim 1, wherein the source fluid pH is adjusted to be in the range of from about 5.0 to about 8.0.
6. The method of claim5, wherein the source fluid pH is adjusted to be in the range of from about 6.0 to about 7.0.

7. The method of claim 1, wherein at least a portion of the suspended metal ion salts are allowed to settle before the salts are separated from the hydraulic fluid.

8. The method of claim4, wherein the oxidizing biocide comprises a material selected from the group consisting of chlorine bleach, peroxides, peracids, persulfates, ozone, chlorine dioxide, and combinations thereof.

9. The method of claim8, wherein the oxidizing biocide comprises chlorine dioxide.

10. The method of claim7, wherein the anionic silica-based colloid comprises a material selected from the group consisting of polysilicic acid, polysilicic acid microgels, polysilicate microgels, polyaluminosilicate microgels, colloidal silicas with a high microgel content, and combinations thereof.

11. The method of claim 1, wherein the oxidizable metal ion salt comprises a material selected from the group consisting of ferrous ion and manganous ion.

12. The method of claim 11, wherein the oxidizable metal ion salt comprises ferrous ion.

13. The method of claim 1, wherein the aqueous, hydraulic fracturing source fluid further comprises at least one material selected from the group consisting of alkali metal salts, alkaline-earth metal salts, friction reducing polymer, scale inhibitor, corrosion inhibitor, hydrocarbon, and proppant.

14. The method of claim 2, wherein the cationic organic polymer comprises a material selected from the group consisting of high molecular weight cationic organic polymers and low molecular weight cationic organic polymers.

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15. The method of claim 14, wherein the cationic organic polymer comprises cationic polyacrylamide.

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# INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/034865

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/66 C02F1/52 C02F1/64 C02F1/72 C02F9/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C02F C09K E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"E" earlier application or patent but published on or after the international filing date

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 20 June 2014 | 30/06/2014 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Redecker, Michael |

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International application No
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