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(54) Title: METHOD FOR ENHANCED FRACTURE CLEANUP USING REDOX TREATMENT

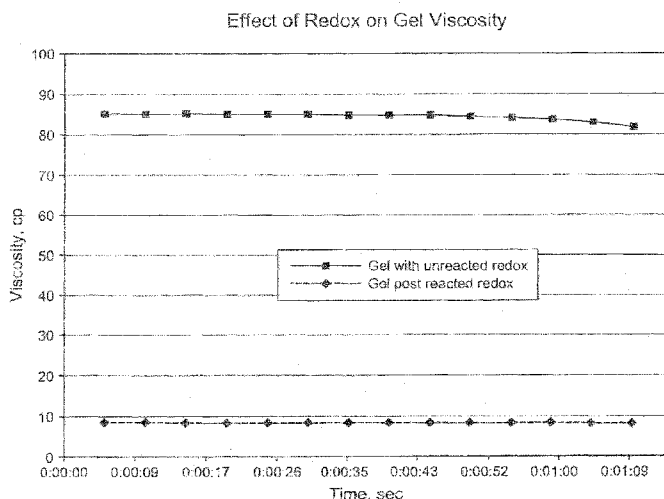


FIG. 1

(57) Abstract: A method for improved hydrocarbon recovery from a formation due to cleanup of a residual viscous material is provided. The method comprising the steps of fracturing the formation with a fracturing fluid to generate fractures, the fracturing fluid comprising a viscous fluid component operable to fracture the formation leaving behind residual viscous material in the fractures, the viscous fluid having a viscosity; a proppant component comprising a proppant, the proppant operable to hold open the fractures, wherein the proppant component is carried to the fractures by the viscous fluid component; and a cleanup fluid, the cleanup fluid comprising: an acid precursor operable to trigger an exothermic reaction component, and the exothermic reaction component operable to generate heat, where the generated heat is operable to reduce a viscosity of the residual viscous material to create a reduced viscosity material operable to flow from the formation.



**PCT PATENT APPLICATION**  
**METHOD FOR ENHANCED FRACTURE CLEANUP**  
**USING REDOX TREATMENT**

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**FIELD**

[0001] This disclosure relates to a composition and method to improve the recovery of hydrocarbons from a fractured formation. More specifically, this disclosure relates to a composition and method to reduce the viscosity of a fracturing fluid.

**BACKGROUND**

[0002] Hydraulic fracturing fluids containing proppants are used extensively to enhance productivity from hydrocarbon reservoir formations, including carbonate and sandstone formations. During hydraulic fracturing operations, a fracturing treatment fluid is pumped under a pressure and rate sufficient for cracking the formation of the reservoir and creating a fracture. Fracturing operations usually consist of three main stages including a pad fluid stage, a proppant fluid stage, and an overflush fluid stage. The pad fluid stage typically consists of pumping a pad fluid into the formation. The pad fluid is a viscous gelled fluid which initiates and propagates the fractures. Auxiliary fractures can propagate from the fractures to create fracture networks. A fracture network can comprise fractures and auxiliary fractures. Auxiliary fractures can connect the fractures.

[0003] The proppant fluid stage involves pumping a proppant fluid into the fractures of the formation. The proppant fluid contains proppants mixed with a viscous gelled fluid or a visco-elastic surfactant fluid. The proppants in the proppant fluid are lodged in the fractures and create conductive fractures through which hydrocarbons flow. The final stage, the overflush stage, includes pumping a viscous, gelled fluid into the fractures to ensure the

proppant fluid is pushed inside the fractures. While the three stages have different aims, all three make use of highly viscous and/or gelled fluids to achieve those aims.

[0004] A downside of the traditional method is that a high volume of gelled or polymeric materials can be left behind in the fractures. The gelled materials can be concentrated around the proppant in the fractures or can be freely in the fractures. The gelled material acts to block the fractures reducing the fracture conductivity. The hydrocarbons which flow from the reservoir formation are unable to move the gelled materials. Traditional methods for cleaning the fractures involve viscosity breakers or other elements to breakdown the fluid. These traditional methods suffer from an inability to completely cleanup the fractures, leaving residual viscous material and reduced conductivity.

### SUMMARY

[0005] This disclosure relates to a composition and method to improve the recovery of hydrocarbons from a fractured formation. More specifically, this disclosure relates to a composition and method to reduce the viscosity of a fracturing fluid, such as, for example, a gelled and/or viscous fracturing fluid.

[0006] In one aspect, a method for improved hydrocarbon recovery from a formation due to cleanup of a residual viscous material is provided. The method includes the step of fracturing the formation with a fracturing fluid to generate fractures. The fracturing fluid includes a viscous fluid component, the viscous fluid component operable to fracture the formation to create fractures leaving behind the residual viscous material in the fractures, the viscous fluid component having a viscosity, a proppant component, the proppant component includes a proppant, the proppant operable to hold open the fractures, wherein the proppant component is carried to the fractures by the viscous fluid component, and a cleanup fluid.

[0007] The cleanup fluid includes an acid precursor, the acid precursor operable to trigger an exothermic reaction component, and the exothermic reaction component operable to generate heat, wherein the heat is operable to reduce a viscosity of the residual viscous material to create a reduced viscosity material, the reduced viscosity material operable to flow from the formation. Fractures can include auxiliary fractures, which propagate from the fractures.

[0008] In certain aspects, the exothermic reaction component includes an ammonium containing compound and a nitrite containing compound. In certain aspects of the present disclosure, the ammonium containing compound is  $\text{NH}_4\text{Cl}$  and the nitrite containing compound is  $\text{NaNO}_2$ . In certain aspects of the disclosure, the acid precursor is triacetin.

[0009] In a second aspect of the present disclosure, a cleanup fluid for reducing a viscosity of a residual viscous material in fractures is provided. The cleanup fluid includes an acid precursor, the acid precursor operable to trigger an exothermic reaction component, and the exothermic reaction component operable to generate heat, wherein the heat is operable to reduce a viscosity of the residual viscous material to create a reduced viscosity material, the reduced viscosity material operable to flow from the fractures.

[0010] In certain aspects, the exothermic reaction component includes an ammonium containing compound and a nitrite containing compound. In certain aspects of the present disclosure, the ammonium containing compound is  $\text{NH}_4\text{Cl}$  and the nitrite containing

compound is  $\text{NaNO}_2$ . In certain aspects of the present disclosure, the acid precursor is triacetin.

[0011] In a third aspect, a method to cleanup fractures post hydraulic fracturing is provided. The method includes the steps of fracturing a formation in a hydraulic fracturing operation to produce fractures, and injecting a cleanup fluid into the fractures to reduce a viscosity of a residual viscous material.

[0012] In certain aspects of the present disclosure, the step of fracturing the formation includes the step of fracturing the formation with a fracturing fluid to generate fractures. The fracturing fluid includes a viscous fluid component, the viscous fluid component operable to fracture the formation to create fractures leaving behind the residual viscous material in the fractures, the viscous fluid component having a viscosity, and a proppant component, the proppant component comprising a proppant, the proppant operable to hold open the fractures, wherein the proppant component is carried to the fractures by the viscous fluid component. In certain aspects of the present disclosure, the cleanup fluid includes an acid precursor, the acid precursor operable to trigger an exothermic reaction component, and the exothermic reaction component operable to generate heat, wherein the heat is operable to reduce a viscosity of the residual viscous material to create a reduced viscosity material, the reduced viscosity material operable to flow from the fractures. In certain aspects of the present disclosure, the exothermic reaction component includes an ammonium containing compound and a nitrite containing compound. In certain aspects, the ammonium containing compound is  $\text{NH}_4\text{Cl}$  and the nitrite containing compound is  $\text{NaNO}_2$ . In certain aspects, the acid precursor is triacetin.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0013] These and other features, aspects, and advantages of the present disclosure will become better understood with regard to the following descriptions, claims, and accompanying drawings. It is to be noted, however, that the drawings illustrate only several embodiments of the disclosure and are therefore not to be considered limiting of the disclosure's scope as it can admit to other equally effective embodiments.

[0014] FIG. 1 is a graphic representation of the effect of the cleanup fluid on the viscosity of the residual viscous material.

[0015] FIG. 2 is a graphic representation of the heat and pressure generated by the exothermic reaction component.

[0016] FIGS. 3a and 3b are pictorial representations of the residual viscous material before the reaction of an exothermic reaction component of the cleanup fluid.

[0017] FIG. 4 is a graphic representation of the effect of the reaction of the exothermic reaction component on the viscosity of a fracturing fluid.

### DETAILED DESCRIPTION

[0018] While the disclosure will be described with several embodiments, it is understood that one of ordinary skill in the relevant art will appreciate that many examples, variations and alterations to the apparatus and methods described herein are within the scope and spirit of the disclosure. Accordingly, the embodiments described herein are set forth without any loss of generality, and without imposing limitations, on the claims.

[0019] In one aspect, a method for improved hydrocarbon recovery from a formation due to cleanup of a residual viscous material is provided. The hydraulic fracturing operation fractures the formation using fracturing fluid to create fractures. Formations include sandstone and carbonate, for example.

[0020] The fracturing fluid includes a viscous fluid component and a proppant component. The viscous fluid component has a viscosity. The viscous fluid component is operable to increase the viscosity of the fracturing fluid. Viscous fluid components include viscosified water-based fluids, non-viscosified water-based fluids, gel-based fluids, gel oil-based fluids, acid-based fluids, and foam fluids. Gel-based fluids include cellulose derivatives and guar-based fluids. Cellulose derivatives include carboxymethyl cellulose, hydroxyethyl cellulose, carboxymethyl hydroxyethyl cellulose, hydroxypropyl cellulose, and methyl hydroxyl ethyl cellulose.

[0021] Guar-based fluids include hydroxypropyl guar, carboxymethyl guar, guar cross-linked boron ions from an aqueous borax/boric acid solution, and guar cross-linked with organometallic compounds. Organometallic compounds include zirconium, chromium, antimony, and titanium salts. Gel oil-based fluids include aluminum phosphate-ester oil gels. In at least one embodiment of the present disclosure, the viscous fluid component is an aqueous guar solution, having a concentration of guar gum between about 0.1% and about 15%, between about 0.1% and about 10%, between about 1% and about 10%, between about 2% and about 8%, and between about 4% and about 6%.

[0022] The proppant component includes a proppant. The proppant is operable to hold open fractures created by the viscous fluid component. Any proppants capable of holding open fractures to create a conductive fractures are suitable for use in the present disclosure. In some embodiments, the proppant component includes a viscous carrier fluid having a viscosity. Viscous carrier fluids include viscosified water-based fluids, non-viscosified water-based fluids, gel-based fluids, gel oil-based fluids, acid-based fluids, and foam fluids.

Gel-based fluids include cellulose derivatives and guar-based fluids. Cellulose derivatives include carboxymethyl cellulose, hydroxyethyl cellulose, carboxymethyl hydroxyethyl cellulose, hydroxypropyl cellulose, and methyl hydroxyl ethyl cellulose.

[0023] Guar-based fluids include hydroxypropyl guar, carboxymethyl guar, guar cross-linked boron ions from an aqueous borax/boric acid solution, and guar cross-linked with organometallic compounds. Organometallic compounds include zirconium, chromium, antimony, and titanium salts. Gel oil-based fluids include aluminum phosphate-ester oil gels. In some embodiments, the hydraulic fracturing operation uses a one stage fracturing fluid, in which the fracturing fluid includes both the viscous fluid component and the proppant component, in which the viscous fluid component carries the proppant component to the fractures.

[0024] In at least one embodiment, the hydraulic fracturing operation uses a multi-stage fracturing fluid in which the viscous fluid component is injected into the formation, followed by the proppant component in the viscous carrier fluid. In some embodiments, the injection of the proppant component is followed by injection of additional viscous fluids to ensure the proppants are placed in the fractures. The additional viscous fluids have a viscosity.

[0025] In some embodiments, the viscosity of the viscous fluid component, the viscous carrier fluid, and additional viscous fluids are the same. In some embodiments, the viscosity of the viscous fluid component, the viscous carrier fluid, and additional viscous fluids are different. The injection of the fracturing fluid ceases after the proppants are placed in the fractures and the fracturing fluid is allowed to seep from the fractures. In some embodiments, the injection of the hydraulic fracturing fluid including the viscous fluid component and/or the proppant component and/or the overflush component and/or the exothermic reaction component does not generate foam or introduce foam into the hydraulic formation including the hydraulic fractures.

[0026] The hydraulic fracturing operation can leave residual viscous material in the fractures of a hydraulic formation. Residual viscous materials can include carboxymethyl cellulose, hydroxyethyl cellulose, carboxymethyl hydroxyethyl cellulose, hydroxypropyl cellulose, methyl hydroxyl ethyl cellulose, guar gum, hydroxypropyl guar, carboxymethyl guar, guar cross-linked with boron, aluminum phosphate-ester oil gel, and guar cross-linked with organometallic compounds. Organometallic compounds include zirconium, chromium, antimony, and titanium salts. In some embodiments of the present disclosure, the residual



viscous material is a gelled material. In some embodiments of the present disclosure, the residual viscous material is a polymeric material. In at least one embodiment of the present disclosure, the residual viscous material is guar gum. The residual viscous material has a viscosity greater than the fracturing fluid. In at least one embodiment of the present disclosure, the residual viscous material is surrounding and/or adjacent to the proppants placed in the fractures.

[0027] The cleanup fluid acts, after the proppants have been placed in the fractures, to remove the residual viscous material. In one embodiment, the cleanup fluid is mixed with the fracturing fluid. In at least one embodiment of the present disclosure, where a multi-stage fracturing fluid is used, the cleanup fluid is a component of the fluids used at each stage of the hydraulic fracturing operation. In an alternate embodiment, the cleanup fluid is added only to the fluid of the final stage of the hydraulic fracturing operation, such as, for example, the overflush stage. In some embodiments, the cleanup fluid is pumped to the fractured formation as a separate step following the hydraulic fracturing operation.

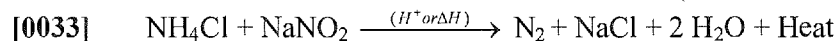
[0028] In some embodiments, the cleanup fluid includes an acid precursor and an exothermic reaction component. The reaction of the exothermic reaction component results in a release of kinetic energy and thermal energy. The reaction of the exothermic reaction component generates heat and increases the pressure. The generated heat increases the temperature of the surrounding fluids, including fracturing fluid remaining in the fractures and residual viscous material. The increase in temperature reduces the viscosity of the fracturing fluid. The increase in temperature reduces the viscosity of the residual viscous material left in the fractures to create a reduced viscosity material. The reduced viscosity material flows from the fractures of the formation to the wellbore. The increase in pressure provides lift energy to push the reduced viscosity materials through the wellbore toward the surface. The removal of the residual viscous material increases the conductivity of the fractures. Increased conductivity of the fractures increases seepage of the fracturing fluid, improves fracturing efficiency, minimizes need for additional fracturing jobs, minimizes time between fracturing and well production, and increases hydrocarbon flow, which translates to increased hydrocarbon recovery.

[0029] The acid precursor is any acid that releases hydrogen ions to trigger the reaction of the exothermic reaction component. Acid precursors include triacetin (1,2,3-triacetoxypropane), methyl acetate, HCl, and acetic acid. In at least one embodiment, the acid precursor is triacetin. In at least one embodiment, the acid precursor is acetic acid.

[0030] The exothermic reaction component includes one or more redox reactants that exothermically react to produce heat and increase pressure. Exothermic reaction components include urea, sodium hypochlorite, ammonium containing compounds, and nitrite containing compounds. In at least one embodiment of the present disclosure, the exothermic reaction component includes ammonium containing compounds. Ammonium containing compounds include ammonium chloride, ammonium bromide, ammonium nitrate, ammonium sulfate, ammonium carbonate, and ammonium hydroxide.

[0031] In at least one embodiment, the exothermic reaction component includes nitrite containing compounds. Nitrite containing compounds include sodium nitrite and potassium nitrite. In at least one embodiment, the exothermic reaction component includes both ammonium containing compounds and nitrite containing compounds. In at least one embodiment, the ammonium containing compound is ammonium chloride,  $\text{NH}_4\text{Cl}$ . In at least one embodiment, the nitrite containing compound is sodium nitrite,  $\text{NaNO}_2$ .

[0032] In at least one embodiment of the present disclosure, the exothermic reaction component includes two redox reactants:  $\text{NH}_4\text{Cl}$  and  $\text{NaNO}_2$ , which react according to the following:



[0034] In a reaction of the exothermic reaction components according to the above equation, generated gas and heat contribute to the reduction of the viscosity of the residual viscous material.

[0035] The exothermic reaction component is triggered to react. In at least one embodiment of the present disclosure, the exothermic reaction component is triggered within the fractures. In at least one embodiment of the present disclosure, the acid precursor triggers the exothermic reaction component to react by releasing hydrogen ions.

[0036] In at least one embodiment, the exothermic reaction component is triggered by heat. The wellbore temperature is reduced during a pre-pad injection or a pre-flush with brine and reaches a temperature below  $120^\circ\text{F}$  ( $48.9^\circ\text{C}$ ). The fracturing fluid of the present disclosure is then injected into the well and the wellbore temperature increases. When the wellbore temperature reaches a temperature greater than or equal to  $120^\circ\text{F}$ , the reaction of the redox reactants is triggered. In at least one embodiment, the reaction of the redox reactants is triggered by temperature in the absence of the acid precursor. In at least one

embodiment, the exothermic reaction component is triggered by heat when the exothermic reaction component is within the fractures.

[0037] In at least one embodiment, the exothermic reaction component is triggered by pH. A base is added to the fracturing fluid of the present disclosure to adjust the pH to between 9 and 12. In at least one embodiment, the base is potassium hydroxide. The fracturing fluid with the base is injected into the formation. Following the injection of the fracturing fluid, an acid is injected to adjust the pH to below 6. When the pH is below 6, the reaction of the redox reactants is triggered. In at least one embodiment, the exothermic reaction component is triggered by pH when the exothermic reaction component is within the fractures.

[0038] In at least one embodiment of the present disclosure, the cleanup fluid is introduced to the fractures following the hydraulic fracturing operation. Dual-string coiled tubing is used to introduce the exothermic reaction component and the acid precursor to the wellbore. In at least one embodiment, the exothermic reaction component includes  $\text{NH}_4\text{Cl}$  and  $\text{NaNO}_2$ . The acid precursor is acetic acid. The acetic acid is mixed with  $\text{NH}_4\text{Cl}$  and injected in parallel with the  $\text{NaNO}_2$ , using different sides of the dual-string coiled tubing. The exothermic reaction component and the acid precursor mix within the fractures.

#### [0039] EXAMPLES

[0040] Example 1. An exothermic reaction component of a cleanup fluid consisting of 3M  $\text{NH}_4\text{Cl}$  and 3M  $\text{NaNO}_2$  was added to a solution of 1% by volume guar at room temperature, see FIG. 3. The exothermic reaction component was triggered by heat. The viscosity of the solution was measured before, during, and after the reaction using a Chandler viscometer. Prior to reaction of the exothermic reaction component, the viscosity of the residual viscous material was 85 cP. FIG. 1 is a graph of the viscosity following the reaction of the exothermic reaction component. The graph shows that the viscosity of the residual viscous material was reduced to less than 8.5 cP. FIG. 3b shows the solution, including the residual viscous material after the reaction of the exothermic reaction component.

[0041] Example 2. A solution of an exothermic reaction component was prepared from 3M  $\text{NH}_4\text{Cl}$  and 3M  $\text{NaNO}_2$ . The solution was placed in an autoclave reactor at room temperature and an initial pressure of 1,000 psi. The reactor temperature was increased. The reaction was triggered at about 120°F, see FIG. 2. Due to the reaction, the temperature in the reactor reached a temperature of 545°F and a pressure of 3,378 psi, see FIG. 2.

[0042] Example 3. The exothermic reaction component showed compatibility with the viscous fluid component (here an x-linked gel). The fracturing fluid with the viscous fluid component, the exothermic reaction component, and the proppant component was also prepared and showed compatibility. The fracturing fluid, without the proppant component, was activated in the autoclave reactor by heating to the wellbore temperature to trigger the reaction of the exothermic reaction component. The heat generated by the reaction reduced the viscosity of the viscous fluid component to produce a reduced viscosity material, without injecting the viscosity breaker. Using a Chandler viscometer, the viscosity of the fracturing fluid, containing the viscous fluid component and the exothermic reaction component, was measured pre-reaction and post-reaction. The viscosity of the fracturing fluid was reduced from 1600 cp to 10 cp, as shown in FIG. 4. The results show that the exothermic reaction component and this type of treatment can clean-up the fractures post a fracturing job.

[0043] Although the present disclosure has been described in detail, it should be understood that various changes, substitutions, and alterations can be made hereupon without departing from the principle and scope of the disclosure. Accordingly, the scope of the present disclosure should be determined by the following claims and their appropriate legal equivalents.

[0044] The singular forms “a,” “an,” and “the” include plural referents, unless the context clearly dictates otherwise.

[0045] Optional or optionally means that the subsequently described event or circumstances can or may not occur. The description includes instances where the event or circumstance occurs and instances where it does not occur.

[0046] Ranges may be expressed herein as from about one particular value, and/or to about another particular value. When such a range is expressed, it is to be understood that another embodiment is from the one particular value and/or to the other particular value, along with all combinations within said range.

[0047] Throughout this application, where patents or publications are referenced, the disclosures of these references in their entireties are intended to be incorporated by reference into this application, in order to more fully describe the state of the art to which the disclosure pertains, except when these references contradict the statements made herein.

[0048] As used herein and in the appended claims, the words “comprise,” “has,” and “include” and all grammatical variations thereof are each intended to have an open, non-limiting meaning that does not exclude additional elements or steps.

[0049] As used herein, terms such as “first” and “second” are arbitrarily assigned and are merely intended to differentiate between two or more components of an apparatus. It is to be understood that the words “first” and “second” serve no other purpose and are not part of the name or description of the component, nor do they necessarily define a relative location or position of the component. Furthermore, it is to be understood that the mere use of the term “first” and “second” does not require that there be any “third” component, although that possibility is contemplated under the scope of the present disclosure.

### CLAIMS

What is claimed is:

1. A method for improved hydrocarbon recovery from a formation due to cleanup of a residual viscous material, the method comprising the steps of:  
fracturing the formation with a fracturing fluid to generate fractures, the fracturing fluid comprising:  
a viscous fluid component, the viscous fluid component operable to fracture the formation to create the fractures leaving behind the residual viscous material in the fractures, the viscous fluid component having a viscosity;  
a proppant component, the proppant component comprising a proppant, the proppant operable to hold open the fractures,  
wherein the proppant component is carried to the fractures by the viscous fluid component; and  
a cleanup fluid, the cleanup fluid comprising:  
an acid precursor, the acid precursor operable to trigger an exothermic reaction component, and  
the exothermic reaction component operable to generate heat,  
wherein the heat is operable to reduce a viscosity of the residual viscous material to create a reduced viscosity material, the reduced viscosity material operable to flow from the formation.
2. The method of claim 1, wherein the exothermic reaction component comprises an ammonium containing compound and a nitrite containing compound.
3. The method of claim 2, wherein the ammonium containing compound comprises  $\text{NH}_4\text{Cl}$  and the nitrite containing compound comprises  $\text{NaNO}_2$ .
4. The method of any one of claims 1-3, wherein the acid precursor comprises triacetin.
5. The method of any one of claims 1-3, wherein the step of fracturing the formation with a fracturing fluid to generate fractures further comprises the step of forming auxiliary fractures and a fracture network.

6. A cleanup fluid for reducing a viscosity of a residual viscous material in fractures, the cleanup fluid comprising:

an acid precursor, the acid precursor operable to trigger an exothermic reaction component; and

the exothermic reaction component operable to generate heat,

wherein the heat is operable to reduce a viscosity of the residual viscous material to create a reduced viscosity material, the reduced viscosity material operable to flow from the fractures.

7. The cleanup fluid of claim 6, wherein the exothermic reaction component comprises an ammonium containing compound and a nitrite containing compound.
8. The cleanup fluid of claim 7, wherein the ammonium containing compound comprises  $\text{NH}_4\text{Cl}$  and the nitrite containing compound comprises  $\text{NaNO}_2$ .
9. The cleanup fluid of any one of claims 6-8, wherein the acid precursor comprises triacetin.
10. A method to cleanup fractures in hydraulic fracturing operations, the method comprising the steps of:  
fracturing a formation in a hydraulic fracturing operation to generate fractures,  
wherein the step of fracturing the formation comprises the step of fracturing the formation with a fracturing fluid to generate fractures, the fracturing fluid comprising:  
a viscous fluid component, the viscous fluid component operable to fracture the formation to create the fractures leaving behind residual viscous material in the fractures, the viscous fluid component having a viscosity;  
a proppant component, the proppant component comprising a proppant, the proppant operable to hold open the fractures, wherein the proppant component is carried to the fractures by the viscous fluid component; and  
injecting a cleanup fluid into the fractures to reduce a viscosity of the residual viscous material.
11. The method of claim 10, wherein the cleanup fluid comprises:

an acid precursor, the acid precursor operable to trigger an exothermic reaction component; and

the exothermic reaction component operable to generate heat,

wherein the heat is operable to reduce a viscosity of the residual viscous material to create a reduced viscosity material, the reduced viscosity material operable to flow from the fractures.

12. The cleanup fluid of claim 11, wherein the exothermic reaction component comprises an ammonium containing compound and a nitrite containing compound.
13. The cleanup fluid of claim 12, wherein the ammonium containing compound comprises  $\text{NH}_4\text{Cl}$  and the nitrite containing compound comprises  $\text{NaNO}_2$ .
14. The cleanup fluid of any one of claims 11-13, wherein the acid precursor comprises triacetin.
15. The method of any one of claims 11-13, wherein the step of fracturing the formation with a fracturing fluid to generate fractures further comprises the step of forming auxiliary fractures and a fracture network.



Effect of Redox on Gel Viscosity

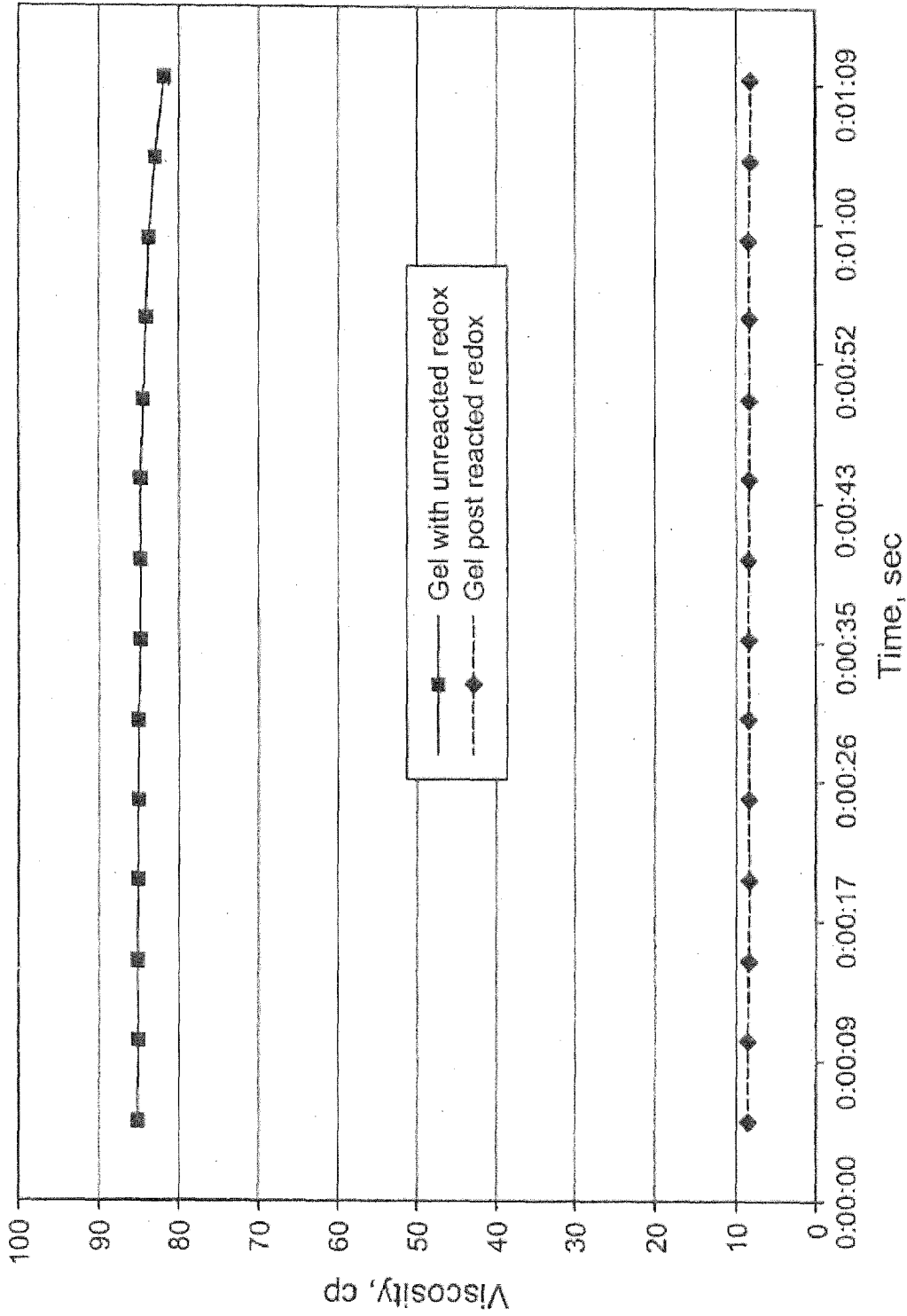


FIG. 1

Redox Reaction

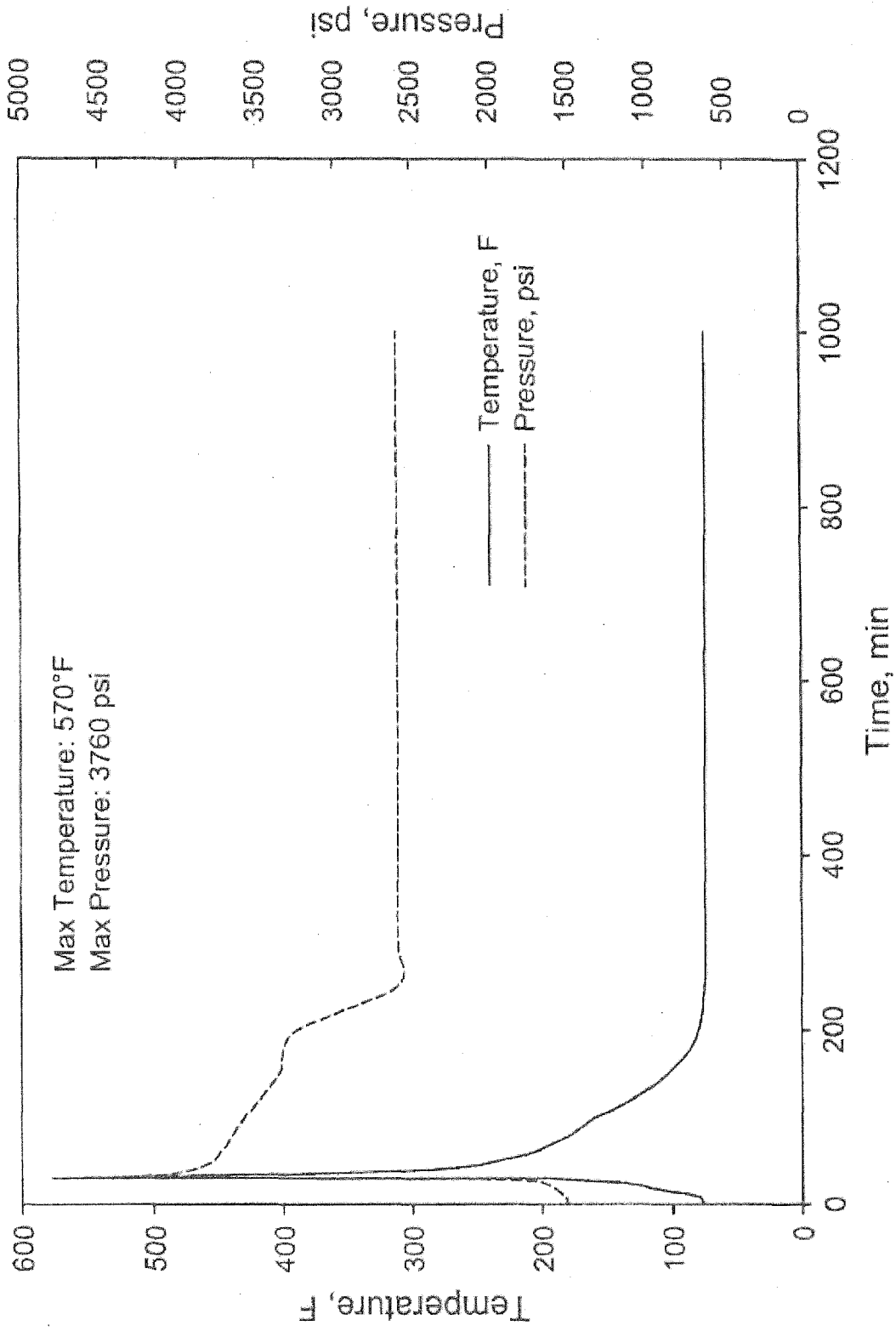


FIG. 2

3/4

Pre Reaction

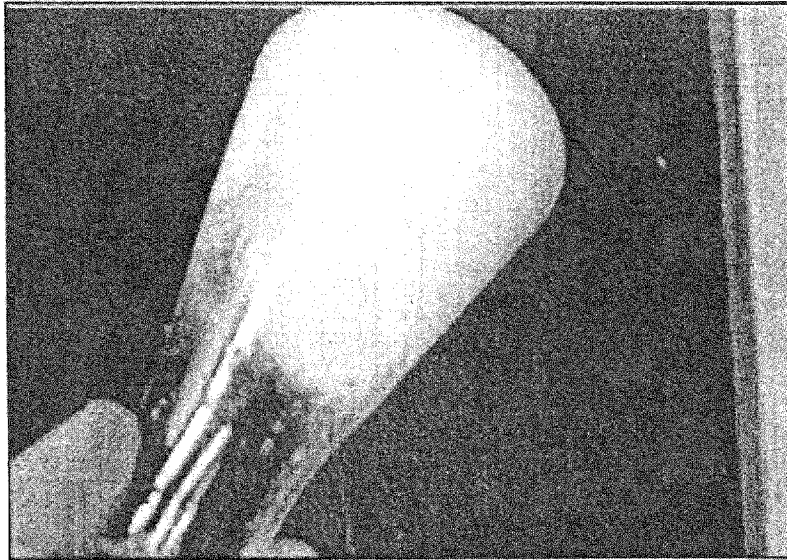


FIG. 3a

Post Reaction

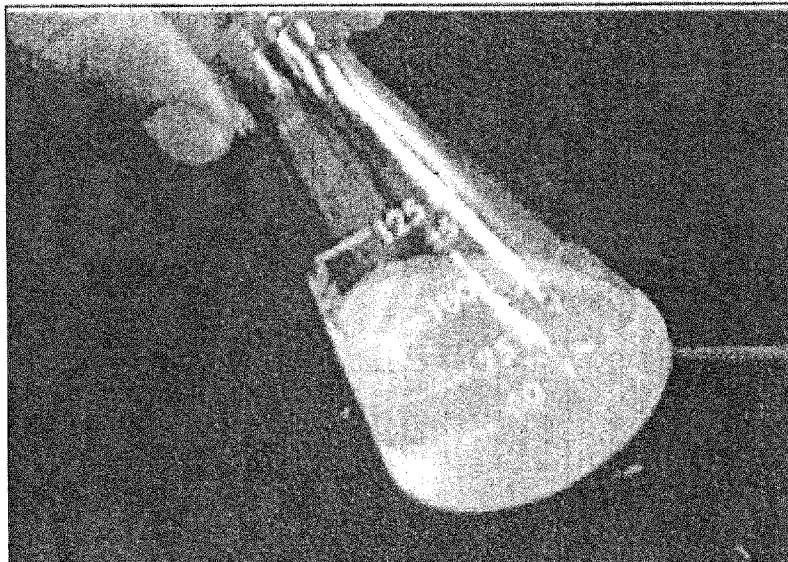


FIG. 3b

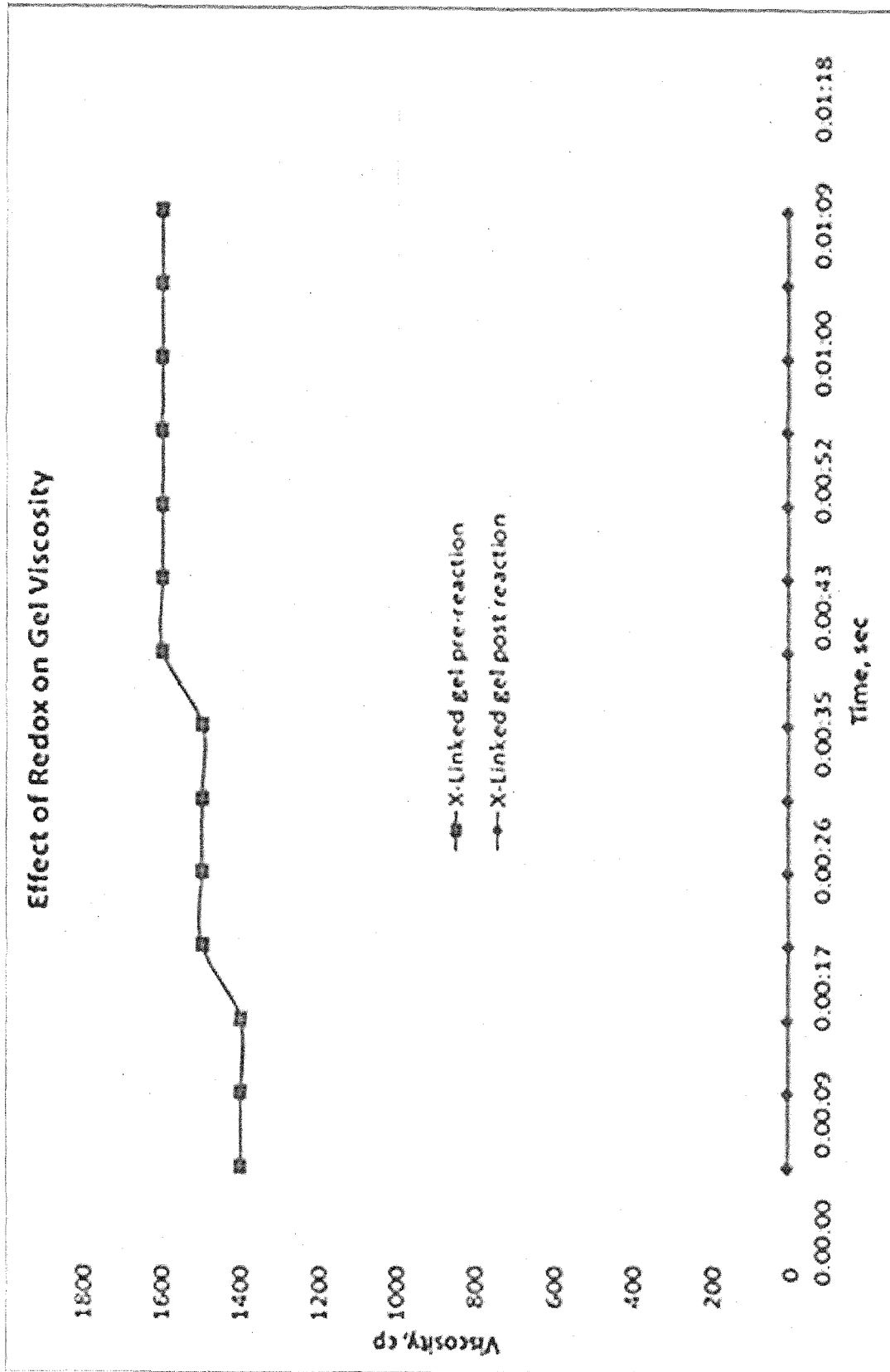


FIG. 4

# INTERNATIONAL SEARCH REPORT

International application No PCT/US2015/026381
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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. C09K8/52      C09K8/592      C09K8/62      E21B43/24 ADD.				
According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b>				
Minimum documentation searched (classification system followed by classification symbols) 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				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.				
* Special categories of cited documents : <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;">                     "A" document defining the general state of the art which is not considered to be of particular relevance                      "E" earlier application or patent but published on or after the international filing date                      "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)                      "O" document referring to an oral disclosure, use, exhibition or other means                      "P" document published prior to the international filing date but later than the priority date claimed                 </td> <td style="width: 50%; border: none; vertical-align: top;">                     "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention                      "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone                      "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art                      "&amp;" document member of the same patent family                 </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
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International application No  
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