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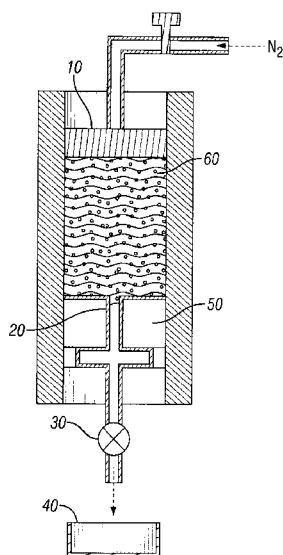
(54) **Title:** STABILIZATION OF CROSS-LINKED GELS DURING DOWNHOLE TREATMENT APPLICATIONS

FIG. 1

(57) **Abstract:** Methods of treating a subterranean formation are disclosed in which a polymer, such as guar, cross-linked by boron-based cross-linker is stabilized. The methods including preparing a treatment fluid containing a particulate material, and a polymer gel cross-linked by borate-based cross-linker, placing the treatment fluid into a subterranean formation via a wellbore, and placing a low viscosity fluid into the wellbore, the low viscosity fluid including stabilization additives in an effective amount to delay or prevent dissolution or dispersion of the polymer gel cross-linked by borate-based cross-linker.



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STABILIZATION OF CROSS-LINKED GELS DURING DOWNHOLE TREATMENT APPLICATIONS

[0001] BACKGROUND

[0002] Hydrocarbons (oil, natural gas, etc.) may be obtained from a subterranean geologic formation (a "reservoir") by drilling a well that penetrates the hydrocarbon-bearing formation. Well treatment methods often are used to increase hydrocarbon production by using a treatment fluid (often introduced at a high fluid pressure) to interact with a subterranean formation in a manner that ultimately increases hydrocarbon flow (for example, oil and/or gas flow) from the formation to the wellbore for removal to the surface.

[0003] Well treatment fluids, particularly those used in hydraulic fracturing, may comprise water- or oil-based fluid incorporating a thickening agent, normally a polymeric material. In order to prevent a resulting fracture from closing upon release of fluid pressure, conventional hydraulic fracturing technologies may use a hard particulate material known as a proppant, which is dispersed in the treatment fluid to be carried into the resulting fracture and deposited therein. The proppant is transported by the fluid from the wellbore to the tip of the fracture and desirably does not settle (the settling of which may jeopardize the treatment and the integrity of the well). To increase the viscosity, and, therefore, the proppant carrying ability of treatment fluids, as well as increase its high temperature stability, cross-linking of the polymeric materials may be employed.

[0004] Conventional hydraulic fracturing technologies include, for example, (i) the use highly viscous cross-linked fluids to enhance proppant transport deeper into a fracture and to prevent proppant settling, (ii) the use of low viscous fluids (for example, slickwater, water, brines, linear gels), which utilize high pumping rate to achieve a high fluid velocity into the fracture to place proppant deeper to the fracture (for example, slickwater jobs), and (iii) the use of high and low viscous fluids in a "hybrid" fracture treatment in which a low viscosity fluid, such as slickwater, may be used for the pad and a cross-linked gel may be used for the proppant laden stages (reverse hybrid fracture treatment, where the cross-linked fluid is pumped ahead of the slickwater stage, have also been used).

[0005] However, the use of low viscosity fracturing fluids comes with an undesired effect of increased rates of proppant sedimentation (for example, due to destabilization of the

cross-linked gel), which does not allow either uniform placement of proppant along the fracture height or far-field delivery of proppant into fracture. For example, use of guar gel cross-linked by boron in combination with low viscosity fluids (such as slickwater or water) can be limited due to diffusion of cross-linking ions from the cross-linked gel to slickwater.

[0006] SUMMARY

[0007] This summary is provided to introduce a selection of concepts that are further described below in the detailed description. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used as an aid in limiting the scope of the claimed subject matter.

[0008] In some embodiments, the methods of the present disclosure for treating a subterranean formation include preparing a treatment fluid containing a particulate material, and a polymer gel cross-linked by borate-based cross-linker, where the polymeric gel includes guar, hydroxypropyl guar and/or carboxymethylhydroxypropyl guar; placing the treatment fluid into a subterranean formation via a wellbore; and placing a low viscosity fluid into the wellbore, the low viscosity fluid including stabilization additives in an effective amount to delay or prevent dissolution or dispersion of the polymer gel cross-linked by borate-based cross-linker.

[0009] BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The manner in which the objectives of the present disclosure and other desirable characteristics may be obtained is explained in the following description and attached drawings in which:

[0011] FIG. 1 schematically illustrates a fluid loss cell used in the Examples;

[0012] FIG. 2A is a photograph of the behavior of pillars after 10 minutes at 95°C with stabilization additives in the clean fluid (left glass) and without stabilization additives in the clean fluid (right glass), FIG. 2B is a photograph of the behavior of pillars after 30 minutes at 95°C with stabilization additives in the clean fluid (left glass) and without stabilization additives in the clean fluid (right glass);

[0013] FIG. 3A is a photograph of the initial behavior of aggregates (at 95°C) containing nitrogen and 5ppa of sand inside clean fluid with dual B³⁺-Zr⁴⁺ cross-linkers, FIG. 3B is a photograph of the behavior of aggregates (after 4 hours at 95°C,) containing nitrogen and 5ppa

of sand inside clean fluid with dual B^{3+} - Zr^{4+} cross-linkers, and FIG. 3C is a photograph of the behavior of aggregates (after 7 hours at 95°C,) containing nitrogen and 5ppa of sand inside clean fluid with dual B^{3+} - Zr^{4+} cross-linkers.

[0014] DETAILED DESCRIPTION

[0015] In the following description, numerous details are set forth to provide an understanding of the present disclosure. However, it may be understood by those skilled in the art that the methods of the present disclosure may be practiced without these details and that numerous variations or modifications from the described embodiments may be possible.

[0016] At the outset, it should be noted that in the development of any such actual embodiment, numerous implementation-specific decisions may be made to achieve the developer's specific goals, such as compliance with system related and business related constraints, which will vary from one implementation to another. Moreover, it will be appreciated that such a development effort might be complex and time consuming but would nevertheless be a routine undertaking for those of ordinary skill in the art having the benefit of this disclosure. In addition, the composition used/disclosed herein can also comprise some components other than those cited. In the summary and this detailed description, each numerical value should be read once as modified by the term "about" (unless already expressly so modified), and then read again as not so modified unless otherwise indicated in context. Also, in the summary and this detailed description, it should be understood that a range listed or described as being useful, suitable, or the like, is intended to include support for any conceivable sub-range within the range at least because every point within the range, including the end points, is to be considered as having been stated. For example, "a range of from 1 to 10" is to be read as indicating each possible number along the continuum between about 1 and about 10. Furthermore, one or more of the data points in the present examples may be combined together, or may be combined with one of the data points in the specification to create a range, and thus include each possible value or number within this range. Thus, (1) even if numerous specific data points within the range are explicitly identified, (2) even if reference is made to a few specific data points within the range, or (3) even when no data points within the range are explicitly identified, it is to be understood (i) that the inventors appreciate and understand that any conceivable data point within the range is to be considered to have been specified, and (ii)

that the inventors possessed knowledge of the entire range, each conceivable sub-range within the range, and each conceivable point within the range. Furthermore, the subject matter of this application illustratively disclosed herein suitably may be practiced in the absence of any element(s) that are not specifically disclosed herein.

[0017] The methods of the present disclosure relate to treating a subterranean formation by introducing a treatment fluid into a subterranean formation via a wellbore, the treatment fluid comprising a particulate material and a gel of a polymeric material (for example, a gel including a galactomannan gum, such as guar and/or substituted guar like hydroxypropyl guar (HPG) and carboxymethylhydroxypropyl guar (CMHPG)) cross-linked by a cross-linker, such as a borate-based cross-linker; and introducing a low viscosity fluid into the wellbore, where the low viscosity fluid contains activating chemicals/stabilization additives (such as B^{3+} -based cross-linking agents, Ti^{4+} -based cross-linking agents, Zr^{4+} -based cross-linking agents, and pH modifiers).

[0018] In some embodiments, the activating chemicals/stabilization additives are present in an effective amount to accomplish a desired function, such as, for example, adjusting the viscosity of the treatment fluid and/or to attenuate or slow down (or even prevent) dissolving and/or dispersion of the gel (for example, a gel cross-linked by borate-based cross-linker).

[0019] During the methods of the present disclosure, the viscosity of the treatment fluid (and by extension the transport properties of the particulate material, such as proppant) may be manipulated by adjusting or controlling the cross-linking of the gel of the treatment fluid by the use activating chemicals/stabilization additives (such as B^{3+} -based cross-linking agents, Ti^{4+} -based cross-linking agents, Zr^{4+} -based cross-linking agents, and pH modifiers). For example, in some embodiments, the methods of the present disclosure, may manipulate/control and/or initiate both (i) reversible cross-linking based upon pH that has been described for boron-based cross-linkers, and (ii) irreversible cross-linking brought about by metal-based cross-linkers (such as titanium (Ti) or zirconium (Zr)).

[0020] In some embodiments, the addition of cross-linking and activating chemicals/stabilization additives to the low viscosity fluids occurs in a manner (such as by including an effective amount of activating chemicals/stabilization additives) to reduce or even prevent the gel of the treatment fluid from dissolving and/or dissociating for a predetermined

amount of time, such as an amount of time in a range of from about 0.1 to about 30 hours, or an amount of time in a range of from about 1.0 to about 12 hours, or an amount of time in a range of from about 1 to about 4 hours.

[0021] The term "activating chemicals/stabilization additives" refers to any chemical or combination of chemicals that can change a chemical reaction parameter (such as, for example, the reaction rate) at a given temperature and/or pressure. In some embodiments, the activating chemicals/stabilization additives may be produced *in situ* by a chemical reaction, such as a chemical reaction that occurs downhole (for example, due to degradation or hydrolysis of one or more of the components of the treatment fluid and/or low viscosity fluid). Examples of activating chemicals/stabilization additives may include cross-linking agents (for example B^{3+} , Ti^{4+} , Zr^{4+} – based cross-linking agents, or chemicals that dissociate into B^{3+} , Ti^{4+} , Zr^{4+} ions), pH changing chemicals: alkalines, strong alkalines (for example, NaOH, KOH) and weak alkalines (for example, $NaCO_3$); acids, strong acids (for example, HCl) weak acids and buffers.

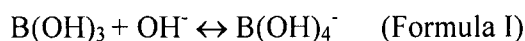
[0022] In some embodiments, the activating chemicals/stabilization additives may include Ti^{4+} , Zr^{4+} –based cross-linking agents or their combination, which, for example, may be added to a low viscosity fluid to provide diffusion of these cross-linking agents from the low viscosity fluid to a cross-linked gel phase and allow cross-linking of a polymeric material (such as, for example, guar) by Ti^{4+} , Zr^{4+} –based cross-linking agents to modify properties of the cross-linked gel (for example, to increase thermo-stability of gel). In some embodiments, stabilization additives may include Ti^{4+} , Zr^{4+} –based cross-linking agents, which, for example, may be added to a low viscosity fluid in combination with additional activating ion generating chemicals to provide cross-linking of polymeric materials (such as, for example, guar) at predetermined pressure/temperature conditions (such as those experienced downhole or those experienced at the surface). In some embodiments, stabilization additives may include Ti^{4+} , Zr^{4+} – based cross-linking agents, which, for example, may be added to a low viscosity fluid in combination with boron-based cross-linking agents and additional activating ions to provide desired cross-linked gel properties at bottomhole conditions. In some embodiments, the stabilization additives may include B^{3+} , Ti^{4+} , Zr^{4+} – based cross-linking agents, which, for example, may be added to a low viscosity fluid in combination with activating ions generating chemicals to provide syneresis of a gel, such as a cross-linked guar gel. In some embodiments, stabilization additives may include B^{3+} , Ti^{4+} , Zr^{4+} – based cross-linking agents, which, for example, may be encapsulated, so the

activating chemicals/stabilization additives can be released in downhole, for example, to a gel cross-linked by boron, and/or a low viscosity fluid phase or to both.

[0023] In the methods of the present disclosure, the activating chemicals/stabilization additives may be added in an amount effective to accomplish a desired downhole function, such as to control and/or adjust properties of the cross-linked gel of the treatment fluid (for example, to increase thermo-stability of the cross-linked gel of the treatment fluid and/or to preserve/maintain the viscosity of a cross-linked phase via stabilization of guar gels cross-linked by boron during hydraulic fracturing in combination with low viscosity fracturing fluids such as slickwater, linear gels, water, produced water or brines).

[0024] In embodiments, the desired downhole function can be accomplished by manipulating the equilibrium of the species/components in the treatment fluid and the low viscosity fluid, such as by monitoring and controlling the concentration of activating chemicals/stabilization additives in the treatment fluid and the low viscosity fluid.

[0025] For example, in embodiments, where the gel comprises cross-linked guar (cross-linked with a B^{3+} -based cross-linking agent, guar and $B(OH)_4^-$ ions do not form permanent covalent bonds, and the amount of available $B(OH)_4^-$ ions is determined, for example, by thermodynamic equilibrium shown in Formula I:



[0026] The equilibrium depicted above can be shifted to the left or right by various factors, such as stimuli like component concentrations and/or pressure. Shifting the equilibrium depicted above to the left may lead to dilution of guar during hybrid treatment (before fracture closure) to the concentration when it can no longer be cross-linked. This causes loss of gel viscosity and its ability to transport proppant during treatment and hold proppant in shut-in conditions (after treatment but before fracture closure). In some embodiments, the methods of the present disclosure avoid that dilution via addition of an effective amount of cross-linking agents and/or activating chemicals/stabilization additives to the low viscosity fluids in a manner to reduce or even prevent the gel from dissolving and/or dissociating.

[0027] For example, in some embodiments, in the methods of the present disclosure borate-based cross-linking and/or activating chemicals/stabilization additives can be added to the

low viscosity fluid in the same concentration as they are present in a cross-linked gel (being introduced into the wellbore). In such embodiments, diffusion of borate-ions and activating OH^- ions from the cross-linked gel to the low viscosity fluid will be prevented. This can be used to increase the time of stability of the gel (for example, the time when a cross-linked gel either does not decrease in viscosity and/or maintains a viscosity level (for example within $\pm 5\%$ of the initial gel viscosity before exposure to the low viscosity fluid) at downhole pressure and temperature conditions). In some embodiments, the time of stability of the gel achieved by the methods of the present disclosure may be an amount of time in a range of from about 0.1 to about 30 hours, or an amount of time in a range of from about 1.0 to about 12 hours, or an amount of time in a range of from about 1 to about 4 hours.

[0028] While the methods of the present disclosure may include introducing a treatment fluid into a subterranean formation via a wellbore, the treatment fluid comprising a particulate material (and optionally fibers and other materials, which may be degradable) and a gel (for example, a gel including a galactomannan gum, such as guar and/or substituted guar such as hydroxypropyl guar (HPG) and carboxymethylhydroxypropyl guar (CMHPG)) cross-linked by borate-based cross-linker, and introducing low viscosity fluid into the wellbore, where the low viscosity fluid contains activating chemicals/stabilization additives (such as B^{3+} -based cross-linking agents, Ti^{4+} -based cross-linking agents, Zr^{4+} -based cross-linking agents, and pH modifiers) in accordance with the methodology of the present disclosure, the methods of the present disclosure otherwise use conventional techniques (such as, for example, hydraulic fracturing techniques) known in the art, such as, for example, methodology described in U.S. Patent Nos. 6,776,235; 7,281,581; 7,213,651; 8,061,424; and 8,205,675; and U.S. Patent Application Publication Nos. 2014/0060828; 2014/0060827; 2014/0060826; and 2014/0054035, the disclosures of which are herein incorporated by reference in their entireties.

[0029] As used herein, the term "treatment fluid," refers to any pumpable and/or flowable fluid used in a subterranean operation in conjunction with a desired function and/or for a desired purpose. In some embodiments, the pumpable and/or flowable treatment fluid may have any suitable viscosity, such as a viscosity of from about 100 cP to about 10000 cP (such as from about 100 cP to about 6000 cP, or from about 100 cP to about 9500 cP) at the treating temperature, which may range from a surface temperature to a bottom-hole static (reservoir) temperature, such as from about 4°C to about 175°C , or from about 10°C to about 135°C , or from

about 20°C to about 121°C, and a shear rate of about 100 s⁻¹ (for the definition of shear rate reference is made to, for example, Introduction to Rheology, Barnes, H.; Hutton, J.F; Walters, K. Elsevier, 1989, the disclosure of which is herein incorporated by reference in its entirety) as measured by common methods, such as those described in textbooks on rheology, including, for example, Rheology: Principles, Measurements and Applications, Macosko, C. W., VCH Publishers, Inc. 1994, the disclosure of which is herein incorporated by reference in its entirety.

[0030] As used herein, the term "low viscosity fluid," refers to a fluid, such as water, slickwater, produced water, brines and/or linear gels, used in a subterranean operation in conjunction with a desired function and/or for a desired purpose. In some embodiments, the low viscosity fluid may have any suitable viscosity, such as a viscosity of from about 0.5 cP to about 50 cP (such as from about 1 cP to about 20 cP, or from about 2 cP to about 10 cP) at the treating temperature, which may range from a surface temperature to a bottom-hole static (reservoir) temperature, and a shear rate of about 100 s⁻¹, or a viscosity of from about 0.5 cP to about 25 cP (such as from about 1 cP to about 20 cP, or from about 2 cP to about 10 cP) at the treating temperature, which may range from a surface temperature to a bottom-hole static (reservoir) temperature, such as from about 1°C to about 175°C, or from about 10°C to about 135°C, or from about 20°C to about 121°C, and a shear rate of about 100 s⁻¹.

[0031] The treatment fluids and/or low viscosity fluids of the present disclosure may be introduced during methods that may be applied at any time in the life cycle of a reservoir, field or oilfield. For example, the methods and treatment fluids and/or low viscosity fluids of the present disclosure may be employed in any desired downhole application (such as, for example, stimulation) at any time in the life cycle of a reservoir, field or oilfield.

[0032] The term "treatment," or "treating," does not imply any particular action by the fluid. For example, a treatment fluid and/or low viscosity fluid may be placed or introduced into a subterranean formation subsequent to a leading-edge fluid may be a hydraulic fracturing fluid, an acidizing fluid (acid fracturing, acid diverting fluid), a stimulation fluid, a sand control fluid, a completion fluid, a wellbore consolidation fluid, a remediation treatment fluid, a cementing fluid, a driller fluid, a frac-packing fluid, or gravel packing fluid. In the methods of the present disclosure, any one of the above fluids may be modified as desired to be suitable for use as a treatment fluid and/or low viscosity fluid. The treatment fluids and/or low viscosity fluids of the

present disclosure may be used in full-scale operations, pills, slugs, pulses or any combination/order thereof. As used herein, a "pill" or "slug" is a type of relatively small volume of specially prepared treatment fluid and/or low viscosity fluid placed or circulated in the wellbore. In some embodiments, the treatment fluids and/or low viscosity fluids of the present disclosure may be used simultaneously.

[0033] In embodiments, the treatment fluids and/or low viscosity fluids of the present disclosure may be formed at the surface and placed/injected or introduced into a wellbore simultaneously, by slugs, by pulses or one after another at any desired volume ratio, such as a volume ratio of the treatment fluid to the low viscosity fluid that is in a range of from about 0.1:99.9 to about 99.9:0.1, such as a range of from about 1:99 to about 99:1, or a range of from about 5:95 to about 95:5, or a range of from about 15:85 to about 85:15; or, in some embodiments, the components of the treatment fluid and/or low viscosity fluids may be separately placed/injected or introduced into a wellbore (such as, for example, via different flow paths, for example, from separate sources, or separate tubing (such as coil tubing), or separately in that one or more components is introduced through the casing and one or more component is separately introduced via coil tubing), or the components of the treatment fluid and/or low viscosity fluids may be simultaneously placed/injected or introduced into a wellbore simultaneously, such as by slugs, by pulses or one after another in any order (and mixed downhole) at any desired volume ratio, such as a volume ratio of the treatment fluid to the low viscosity fluid that is in a range of from about 0.1:99.9 to about 99.9:0.1, such as a range of from about 1:99 to about 99:1, or a range of from about 5:95 to about 95:5, or a range of from about 15:85 to about 85:15.

[0034] As used herein, the term "treating temperature," refers to the temperature of the treatment fluid and/or low viscosity fluid that is observed while the treatment fluid and/or low viscosity fluid is performing its desired function and/or desired purpose, such as fracturing a subterranean formation.

[0035] A "wellbore" may be any type of well, including, a producing well, a non-producing well, an injection well, a fluid disposal well, an experimental well, an exploratory deep well, and the like. Wellbores may be vertical, horizontal, deviated some angle between

vertical and horizontal, and combinations thereof, for example a vertical well with a non-vertical component.

[0036] The term "field" includes land-based (surface and sub-surface) and sub-seabed applications. The term "oilfield," as used herein, includes hydrocarbon oil (for example, black oil and volatile oil), and gas reservoirs (for example, dry gas, wet gas, and retrograde gas), and formations or portions of formations where hydrocarbon oil and gas are expected but may additionally contain other materials such as water, brine, or some other composition.

[0037] The term "fracturing" refers to the process and methods of breaking down a geological formation and creating a fracture, such as the rock formation around a wellbore, by pumping a treatment fluid and/or low viscosity fluid at very high pressures (pressure above the determined closure pressure of the formation), in order to increase production rates from or injection rates into a hydrocarbon reservoir. The fracturing methods of the present disclosure may include introducing one or more treatment fluids and/or low viscosity fluids of the present disclosure, but otherwise use conventional techniques and components known in the art of treating subterranean formations (for example, by hydraulic fracturing), such as, for example, as described in U.S. Patent Nos. 6,776,235; 7,281,581; 7,213,651; 7,581,590; 8,061,424; and 8,205,675; and U.S. Patent Application Publication Nos. 2008/0149329; 2013/0105166; 2014/0060828; 2014/0060827; 2014/0060826; 2014/0054035, the disclosures of which are herein incorporated by reference in their entireties.

[0038] The polymer to be cross-linked (which forms the gel of the present disclosure) may be a polysaccharide or chemically modified polysaccharide in which case the functional groups for attaching to hydroxyl groups of the polymer may be a boron containing cross-linker or "borate-based cross-linker." In some embodiments, a polysaccharide to be cross-linked may be a galactomannan gum, such as guar. Various chemical modifications of guar are available and may be used. One is the introduction of hydroxyl-alkyl substituent groups, such as hydroxypropyl. Another substituent group is carboxyalkyl, such as carboxymethyl. Other polysaccharides (that chemically modified with hydroxyalkyl or carboxyalkyl groups), which may be used in embodiments, include xanthan, scleroglucan, diutan and cellulose.

[0039] In some embodiments, (such as where the gel comprises cross-linked guar or some other polysaccharide or a chemically modified form of guar or other polysaccharide), the

cross-linker may be a borate-based cross-linker (such as, for example, a B^{3+} -based cross-linking agent, or a borate releasing compound, such as boric acid, boron salts, and organic boron compounds) and/or may be a metal cross-linking agent, such as zirconium (such as, for example, Zr^{4+} -based cross-linking agents, or compounds that serve as a source of zirconium IV ions, such as zirconium chelates or complexes) or titanium (such as, for example, Ti^{4+} -based cross-linking agents, or compounds that serve as a source of titanium IV ions, such as titanium chelates).

[0040] In some embodiments, the borate-based cross-linking agents and activating chemicals/stabilization additives may be added to the low viscosity fluid in different concentrations (for example, higher or lower by any desired level effective to perform the intended down hole function, such as maintaining a viscosity level of a gel, increasing a viscosity level of a gel or decreasing viscosity level of the gel) than that of the cross-linked gel. In such embodiments, concentrations of cross-linking ions and activating ions in the gel and in the low viscosity fluids can be selected accordingly to accomplish the intended downhole operation.

[0041] For example, if a cross-linked gel is to be used with slickwater for splitstream operations, a gel would desirably reach full cross-linking before it reaches a merge point (of the treatment fluid containing the gel and the low viscosity fluid), otherwise it will be dissolved. However, the gel should also be formed or designed to be stable enough at the bottomhole conditions. In such embodiments, the methods of the present disclosure may comprise adding borate ion generating compounds and OH^- ions generating compounds to the low viscosity fluid in order to provide diffusion of additional ions to the gel to improve the bottomhole stability of the cross-linked gel and/or prevent the diffusion of the cross-linking moieties out of the cross-linked gel.

[0042] For example, Ti^{4+} , Zr^{4+} -based cross-linking agents and/or additional activating chemicals/stabilization additives may be added to the low viscosity fluid at concentration effective to result in diffusion of these chemicals (and/or ions generated therefrom) into the gel to provide additional cross-linking of gel by these chemicals at bottomhole conditions. In some embodiments, borate-based cross-link agents, Ti^{4+} , Zr^{4+} -based cross-linking agents and activating chemicals/stabilization additives may be added to the low viscosity fluid at concentrations effective to provide syneresis of the gel and tightening of gel-containing proppant aggregates.

[0043] In some embodiments, the concentration of boron in the treatment fluid and/or the low viscosity fluid may be at any desired concentration, such as a concentration in a range of from about 0.5 ppm to about 20 ppt elemental boron (in any state, whether charged or not), such as in a range of from about 10 ppm to about 10 ppt elemental boron, or in a range of from about 100 ppm to about 50 ppt elemental boron. In some embodiments, the concentration of metal (such as zirconium and/or titanium), the concentration of this metal in the treatment fluid and/or the low viscosity fluid may be in a range from about 0.5 ppm to about 50 ppt by weight elemental metal (in any state, whether charged or not), such as in a range of from about 10 ppm to about 20 ppt elemental metal, or in a range of from about 100 ppm to about 10 ppt elemental metal. In embodiments where boron and one or more metals are present the total concentration of all the cross-linking agents together may be at any desired value, such as a total concentration of elemental boron and/or elemental metal in a range of from about 0.5 ppm to about 50 ppt, or a total concentration of elemental boron and/or elemental metal in a range of from about 2 ppm to about 10 ppt.

[0044] In some embodiments, the activating chemicals/stabilization additives may be added to the low viscosity fluid at a concentration that is higher than the concentration of activating chemicals/stabilization additives that are present in the treatment fluid (and/or the gel of the treatment fluid, such as a gel cross-linked by boron), such that diffusion of the activating chemicals/stabilization additives from the low viscosity fluid to the treatment fluid (to the gel of the treatment fluid, such as a gel cross-linked by boron) occurs. In some embodiments, the activating chemicals/stabilization additives may be added to the low viscosity fluid at a concentration that is lower than the concentration of activating chemicals/stabilization additives present in the treatment fluid (and/or the gel of the treatment fluid, such as a gel cross-linked by boron), such that diffusion of the activating chemicals/stabilization additives from the treatment fluid (to the gel of the treatment fluid, such as a gel cross-linked by boron) to the low viscosity fluid occurs.

[0045] In some embodiments, the activating chemicals/stabilization additives may be borate ion generating chemicals and/or activating ion generating chemicals that are added to the low viscosity fluid in the same concentration as that of each respective borate ion generating chemical and/or activating ion generating chemical present in the treatment fluid (the gel of the treatment fluid, such as a gel cross-linked by boron), such that diffusion of borate ion generating

chemicals and/or activating ion generating chemicals (such as borate ions and/or activating ions) from the low viscosity fluid to the treatment fluid (the gel of the treatment fluid) is prevented.

[0046] In some embodiments, the activating chemicals/stabilization additives may be borate ion generating chemicals and/or activating ion generating chemicals that are added to the low viscosity fluid at a concentration that is different from that of each respective borate ion generating chemical and/or activating ion generating chemical present in the treatment fluid (the gel of the treatment fluid, such as a gel cross-linked by boron), such that properties of the treatment fluid (the gel of the treatment fluid, such as a gel cross-linked by boron) are effective to achieve stability (such as less than 5% dissolution/dispersion for a predetermined amount of time, such a time in a range of from about 1 minute to about 120 hours) at the bottomhole conditions, and/or effective to achieve rapid cross-linking (such as achieving a 95% cross-linked gel within a predetermined amount of time, such a time in a range of from about 1 minute to about 120 hours).

[0047] In some embodiments, stabilization additives may comprise borate ion generating chemicals, and the borate ion generating chemicals are added to the low viscosity fluid at a concentration that is higher than the concentration of borate ion generating chemicals present in the treatment fluid (and/or the gel of the treatment fluid, such as a gel cross-linked by boron), such that diffusion of the borate ion generating chemicals (such as borate ions) from the low viscosity fluid to the treatment fluid (and/or the gel of the treatment fluid, such as a gel cross-linked by boron) occurs.

[0048] In some embodiments, the stabilization additives may comprise borate ion generating chemicals, and the borate ion generating chemicals are added to the low viscosity fluid at a concentration that is lower than the concentration of borate ion generating chemicals present in the treatment fluid (and/or the gel of the treatment fluid, such as a gel cross-linked by boron), such that diffusion of the borate ion generating chemicals (such as borate ions) from the treatment fluid (and/or the gel of the treatment fluid, such as a gel cross-linked by boron) to the low viscosity fluid occurs.

[0049] In embodiments, any desired particulate material may be used in the methods of the present disclosure, provided that it is compatible with the formation, the fluid, and the desired results of the treatment operation. For example, particulate materials may include sized sand,

synthetic inorganic proppants, coated proppants, uncoated proppants, resin coated proppants, and resin coated sand.

[0050] In embodiments where the particulate material is a proppant, the proppant used in the methods of the present disclosure may be any appropriate size to prop open the fracture and allow fluid to flow through the proppant pack, that is, in between and around the proppant (which may have been incorporated into a bulky fibrous flock) making up the pack. In some embodiments, the proppant may be selected based on desired characteristics, such as size range, crush strength, and insolubility. In embodiments, the proppant may have a sufficient compressive or crush resistance to prop the fracture open without being deformed or crushed by the closure stress of the fracture in the subterranean formation. In embodiments, the proppant may not dissolve in treatment fluids commonly encountered in a well.

[0051] Suitable proppants may be natural or synthetic (including silicon dioxide, sand, nut hulls, walnut shells, bauxites, sintered bauxites, glass, natural materials, plastic beads, particulate metals, drill cuttings, ceramic materials, and any combination thereof), coated, or contain chemicals; more than one may be used sequentially or in mixtures of different sizes or different materials. The proppant may be resin coated, provided that the resin and any other chemicals in the coating are compatible with the other chemicals of the present disclosure.

[0052] The proppant used may have an average particle size of from about 0.15 mm to about 2.39 mm (about 8 to about 100 U.S. mesh), or of from about 0.25 to about 0.43 mm (40/60 mesh), or of from about 0.43 to about 0.84 mm (20/40 mesh), or of from about 0.84 to about 1.19 mm (16/20), or of from about 0.84 to about 1.68 mm (12/20 mesh) and or of from about 0.84 to about 2.39 mm (8/20 mesh) sized materials. The proppant may be present in a slurry (which may be added to the treatment fluid) in a concentration of from about 0.06 to about 3 kg/L, or about 0.12 to about 1.44 kg/L (about 0.5 PPA to about 25 PPA, or from about 1 to about 12 PPA; PPA is "pounds proppant added" per gallon of liquid).

[0053] In some embodiments, a fibrous material may also be included in the treatment fluid. The additional fibrous material may be one or more member selected from degradable fibers, natural fibers, synthetic organic fibers, glass fibers, ceramic fibers, carbon fibers, inorganic fibers, metal fibers, and a coated form of any of the above fibers. The fiber thickness (diameter), density and concentration may be any suitable value that is effective to assist in the

oilfield operation. As used herein, the term "degradable" means any instance in which the integrity of the fiber or composition thereof is compromised (for example, due to the composition dissolving (partial or complete dissolution), and/or breaking apart into multiple pieces, and/or eroding by physical abrasion, chemical reactions, or a combination of physical abrasion and chemical reactions).

[0054] In some embodiments, the fibers may be pumped with a particulate material, such as proppant, such that the fibers are uniformly mixed with the particulate material. In some embodiments, a dispersion of the fibers and the proppant, which may be in the form of aggregates, may be introduced, such as by pumping, into the subterranean formation. The terms "dispersion" and "dispersed" refer, for example, to a substantially uniform distribution of components in a mixture. In some embodiments, a dispersed phase of one or more fibers and particulate material may be formed at the surface. An action or event occurring "at the surface" refers, for example, to an action or event that happens above ground, that is, not at an underground location, such as within the wellbore or within the subterranean formation.

[0055] In some embodiments, the fibers may be mixed and dispersed throughout the entire batch of proppant to be pumped into the wellbore during the treatment operation. This may occur by adding the fibers to the proppant before it is mixed with the gel of the treatment fluid, adding the fibers to the gel of treatment fluid before it is mixed with the proppant, or by adding a slurry of fibers at some other stage, such either before the slurry is pumped downhole, or at a location downhole.

[0056] In some embodiments, the fibers (or any other degradable materials) may present in the treatment fluid and/or the low viscosity fluid in an amount in the range of from 0 to about 80 ppt, such as in an amount in the range of from 2 ppt to about 40 ppt, or in the range of from about 0.2 to about 2% by weight of the treatment fluid and/or the low viscosity fluid.

[0057] In some embodiments, the methods of the present disclosure may include the following actions, in any order: placing a treatment fluid and a low viscosity fluid into a subterranean formation via a wellbore. The terms "placing" or "placed" refer to the addition of a treatment fluid and/or a low viscosity fluid to a subterranean formation by any suitable means and, unless stated otherwise, do not imply any order by which the actions occur. The term "introduced" refers when used in connection with the addition of a treatment fluid to a

subterranean formation may imply an order of accomplishing the recited actions, if not stated otherwise.

[0058] In some embodiments, a carrier solvent (or carrier fluid) for the treatment fluid and/or the low viscosity fluid may be a pure solvent or a mixture. Suitable solvents for use with the methods of the present disclosure, such as for forming the treatment fluids and/or low viscosity fluids disclosed herein, may be aqueous or organic based. Aqueous solvents may include at least one of fresh water, sea water, brine, mixtures of water and water-soluble organic compounds and mixtures thereof. Organic solvents may include any organic solvent that is able to dissolve or suspend the various components, such as the chemical entities and/or components of the treatment fluid. Suitable organic solvents may include, for example, alcohols, glycols, esters, ketones, nitrites, amides, amines, cyclic ethers, glycol ethers, acetone, acetonitrile, 1-butanol, 2-butanol, 2-butanone, t-butyl alcohol, cyclohexane, diethyl ether, diethylene glycol, diethylene glycol dimethyl ether, 1,2-dimethoxy-ethane (DME), dimethylether, dibutylether, dimethyl sulfoxide (DMSO), dioxane, ethanol, ethyl acetate, ethylene glycol, glycerin, heptanes, hexamethylphosphorous triamide (HMPT), hexane, methanol, methyl t-butyl ether (MTBE), N-methyl-2-pyrrolidinone (NMP), nitromethane, pentane, petroleum ether (ligroine), 1-propanol, 2-propanol, pyridine, tetrahydrofuran (THF), toluene, triethyl amine, o-xylene, m-xylene, p-xylene, ethylene glycol monobutyl ether, polyglycol ethers, pyrrolidones, N-(alkyl or cycloalkyl)-2-pyrrolidones, N-alkyl piperidones, N, N-dialkyl alkanolamides, N,N,N',N'-tetraalkyl ureas, dialkylsulfoxides, pyridines, hexaalkylphosphoric triamides, 1,3-dimethyl-2-imidazolidinone, nitroalkanes, nitro-compounds of aromatic hydrocarbons, sulfolanes, butyrolactones, alkylene carbonates, alkyl carbonates, N-(alkyl or cycloalkyl)-2-pyrrolidones, pyridine and alkylpyridines, diethylether, dimethoxyethane, methyl formate, ethyl formate, methyl propionate, acetonitrile, benzonitrile, dimethylformamide, N-methylpyrrolidone, ethylene carbonate, dimethyl carbonate, propylene carbonate, diethyl carbonate, ethylmethyl carbonate, dibutyl carbonate, lactones, nitromethane, nitrobenzene sulfones, tetrahydrofuran, dioxane, dioxolane, methyltetrahydrofuran, dimethylsulfone, tetramethylene sulfone, diesel oil, kerosene, paraffinic oil, crude oil, liquefied petroleum gas (LPG), mineral oil, biodiesel, vegetable oil, animal oil, aromatic petroleum cuts, terpenes, mixtures thereof.

[0059] In some embodiments, the carrier fluid may be a low viscosity fluid, such as slickwater, which may or may not contain a viscosifying agent, and a sufficient amount of a

friction reducing agent, such as, for example, to minimize tubular friction pressures. In some embodiments, treatment fluids and/or low viscosity fluids comprising a slickwater carrier fluid may have a viscosity that is slightly higher than unadulterated fresh water or brine.

[0060] In some embodiments, the treatment fluid may comprise a linear gel (such as, for example, the carrier fluid) or a linear gel system, which may be cross-linked during the methods of the present disclosure. In some embodiments of the methods of the present disclosure, the low viscosity fluid may include a cross-linked linear gel or a cross-linked linear gel system. Suitable linear gel systems (which may be cross-linked, such as prior to contact with a low viscosity fluid of the present disclosure) may contain carbohydrate polymers such as guar, hydroxyethylcellulose, hydroxyethyl guar, hydroxypropyl guar, and hydroxypropylcellulose. Such linear gel polymers may be added in any desirable amount, such as at about 10 to about 50 pounds of polymer per 1000 gallons of linear gel fluid.

[0061] While the treatment fluids of the present disclosure are described herein as comprising the above-mentioned components, it should be understood that the treatment fluids and/or low viscosity fluids of the present disclosure may optionally comprise other chemically different materials. In embodiments, the treatment fluid and/or low viscosity fluids may further comprise stabilizing agents, surfactants, diverting agents, or other additives. Additionally, a treatment fluid and/or low viscosity fluid may comprise a mixture of various cross-linking agents, and/or other additives, such as fibers or fillers, provided that the other components chosen for the mixture are compatible with the intended use of the treatment fluid and/or low viscosity fluid. Furthermore, the treatment fluid and/or low viscosity fluid may comprise buffers, pH control agents, and various other additives added to promote the stability or the functionality of the treatment fluid and/or low viscosity fluid. The components of the treatment fluid and/or low viscosity fluid may be selected such that they may or may not react with the subterranean formation that is to be treated.

[0062] In this regard, the treatment fluid and/or low viscosity fluid may include components independently selected from any solids, liquids, gases, and combinations thereof, such as slurries, gas-saturated or non-gas-saturated liquids, mixtures of two or more miscible or immiscible liquids, and the like. For example, the treatment fluid and/or low viscosity fluid may comprise organic chemicals, inorganic chemicals, and any combinations thereof. Organic

chemicals may be monomeric, oligomeric, polymeric, cross-linked, and combinations, while polymers may be thermoplastic, thermosetting, moisture setting, elastomeric, and the like. Inorganic chemicals may be metals, alkaline and alkaline earth chemicals, minerals, and the like.

[0063] Typical stabilizing agents may include buffering agents, such as agents capable of buffering at pH of about 8.0 or greater (such as water-soluble bicarbonate salts, carbonate salts, phosphate salts, or mixtures thereof, among others); and chelating agents (such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), or diethylenetriaminepentaacetic acid (DTPA), hydroxyethylethylenediaminetriacetic acid (HEDTA), or hydroxyethyliminodiacetic acid (HEIDA), among others). Buffering agents may be added to the treatment fluid and/or low viscosity fluid in an amount of at least about 0.05 wt%, such as from about 0.05 wt% to about 10 wt%, and from about 0.1 wt% to about 2 wt%, based upon the total weight of the treatment fluid. Chelating agents may be added to the treatment fluid and/or low viscosity fluid in an amount of at least about 0.75 mole per mole of metal ions expected to be encountered in the downhole environment, such as at least about 0.9 mole per mole of metal ions, based upon the total weight of the treatment fluid.

[0064] In some embodiments, it may be desired to foam the treatment fluid and/or the low viscosity fluid using a gas, such as air, nitrogen, methane, natural gas, carbon dioxide or mixture thereof. In some embodiments, the gas may be present in the foamed treatment fluid and/or the foamed low viscosity fluid in an amount in the range of from about 0% to about 80%, from about 2% to about 70%, from about 5% to about 60%, from about 10% to about 50% and from about 20% to about 50% by volume of the foamed treatment fluid and/or the foamed low viscosity fluid. Additional additives such as a surfactants and foaming additives may also be included.

[0065] In some embodiments, the treatment fluid may comprises one or more surfactants at any desired and/or effective concentration for the intended function, such as at a concentration in a range of from about 0 to about 50 gpt, or a concentration in a range of from about 0 to about 20 gpt, or a concentration in a range of from about 2 to about 10 gpt.

[0066] In embodiments, the treatment fluid and/or low viscosity fluid may be driven into a wellbore by a pumping system that pumps one or more treatment fluids and/or low viscosity fluids into the wellbore. The pumping systems may include mixing or combining devices,

wherein various components, such as fluids, solids, and/or gases maybe mixed or combined prior to being pumped into the wellbore. The mixing or combining device may be controlled in a number of ways, including, for example, using data obtained either downhole from the wellbore, surface data, or some combination thereof.

[0067] Fracturing a subterranean formation may include introducing hundreds of thousands of gallons of treatment fluid and/or low viscosity fluid into the wellbore. In some embodiments a frac pump may be used for hydraulic fracturing. A frac pump is a high-pressure, high-volume pump, such as a positive-displacement reciprocating pump. In embodiments, a treatment fluid and/or low viscosity fluid may be introduced by using a frac pump, such that the treatment fluid and/or low viscosity fluid may be pumped down into the wellbore at high rates and pressures, for example, at a flow rate in excess of about 20 barrels per minute (about 4,200 U.S. gallons per minute) at a pressure in excess of about 2,500 pounds per square inch ("psi"). In some embodiments, the pump rate and pressure of the treatment fluid and/or low viscosity fluid may be even higher, for example, at flow rates in excess of about 100 barrels per minute and pressures in excess of about 10,000 psi may be used.

[0068] The foregoing is further illustrated by reference to the following examples, which are presented for purposes of illustration and are not intended to limit the scope of the present disclosure.

[0069] EXAMPLES

[0070] Example 1: Diffusion of activating ions

[0071] In this Example, a treatment fluid was prepared with a composition that set forth in Table 1 (below). OH⁻ ions were used to activate cross-linking of guar by boron. Diffusion of ions between low viscosity fluid and cross-linked gel was used to affect properties of cross-linked gel. In this regard, several tests were conducted in order to test diffusion of OH⁻ ions from the low viscosity fluid to guar gel cross-linked by boron. Compositions of the gel and of the low viscosity fluid used for these experiments are set forth in Tables 1 and 2 (below).

Table 1: Composition of Guar gel cross-linked by boron used for the experiments.

	Guar gum	Boric acid (2 wt.%)	NaOH (5 wt. %)
X-linked gel	35 ppt	52.8 ml/l	2.8 ml/l

Table 2: Composition of the low viscosity fluid used for the experiments.

	Boric acid	NaOH
Low viscosity fluid	1.11 ppt	2.21 ppt

[0072] pH of the both fluids was measured right after preparation of the fluids and after some time when a piece of gel was dropped into the low viscosity fluid. Volumetric ratio of phases was 30:70 (cross-linked gel:low viscosity fluid). Experiments were conducted at ambient temperature and at 60°C. Results are presented in the Table 3.

Table 3: pH changes of low viscosity fluid and guar gel cross-linked by borate-based cross-linker after the contact.

Exp.	Fluid composition	Type of contact	Temperature	Initial pH	pH after contact	pH difference
1	X-linked gel	24 hours, static	Ambient	8.6	9.7	+1.1
	Low viscosity fluid			12.0	10.3	-1.7
2	X-linked gel	15 min, static	Ambient	8.8	8.9	+0.1
	Low viscosity fluid			12.2	12.0	-0.2
3	X-linked gel	After 15 min of handshake	Ambient	8.9	9.8	+1.1
	Low viscosity fluid			12.1	10.4	-1.7
4	X-linked gel	15 min, static	60°C	8.7	9.5	+0.8
	Low viscosity fluid			11.8	10.1	-1.7
5	X-linked gel	24 hours, static	60°C	9.3	9.7	+0.4
	Low viscosity fluid			12.2	10.2	-2.0

[0073] Results show that migration of OH⁻ is observed when guar gel cross-linked by borate-based cross-linker and low viscosity fluid are in contact and if the respective pH of each

fluid is different at the initial stage. This migration leads to a decrease of pH difference between fluids. Shaking promotes this diffusion (as seen by a comparison of the pH difference #3 with #2 and #1). Increase of temperature promotes diffusion of OH⁻ ions at least in initial stage.

[0074] Example 2: Impact of presence of stabilization additives in the low viscosity fluid on ability of guar gel cross-linked by boron to hold sand in dynamic conditions

[0075] To simulate behavior of guar gel cross-linked by boron with low viscosity fluid at high shear conditions, some experiments were conducted with fluid loss cell (FIG.1). The fluid loss cell includes a piston 10, a 2 mm slit 20, a bottom valve 30, a vessel 40, a high shear region 50, and pillar 60 in water (50/50 vol/vol). Pillar with composition given in the Table 4 was loaded with low viscosity fluid at volumetric ratio 50/50 to the chamber and mixture was pressurized with 100 psi.

Table 4: Composition of pillars used to check ability of cross-linked gel to hold sand at high shear conditions.

Guar gum	Sand 100-mesh	3M HGS8000x	Sorbitol	Typical borate-based cross-linker J610 commercially available from Schlumberger
25 ppt	1 ppa	0.42 ppa	30ppt	2 gpt

[0076] Next, the valve located at the bottom of the cell was open and fluid coming out of the cell was caught. Sand that had fallen out of the aggregates was collected, dried and its mass was measured. Experiments were performed when low viscosity fluid did not contain any stabilization additives (where 26% percent of the sand had fallen out of the guar gel cross-linked by boron when it was in contact with low viscosity fluid) and when low viscosity fluid contained 2 gpt of commercially available borate-based cross-linker J610 (where 13% percent of the sand had fallen out of the guar gel cross-linked by boron when it was in contact with low viscosity fluid). Low viscosity fluid was a solution of commercially available (friction reducer B315) in tap water with concentration 0.5 gpt. The results reflect that the amount of sand that had fallen out of the guar gel cross-linked by boron decreases when stabilization additives are present in the low viscosity fluid.

[0077] Example 3: Stabilisation of guar gel, cross-linked by boron by presence of borate ions and OH ions in the low viscosity fluid

[0078] *Ambient temperatures*

[0079] Aggregates based on guar gel cross-linked by boron were dropped to tap water, slickwater and tap water which contained 2 ml of mixture of boric acid and NaOH at room temperature. Aggregates had the same as described in Table 4. Aggregates were left for 3 hours. After this the sand that had fallen out of the aggregates was collected and its amount was measured. The results are in Table 5.

Table 5: Amount of sand fallen out of the aggregates containing 1ppa of sand and 0.42 ppa of HGS8000x after 3hours of contact with low viscosity fluid.

Media	pH	Sand fallen out,
Tap water	7,4	100
Slickwater (0.5 gpt	7,6	95
Tap water + 2 gpt of typical borate-based cross-linker J610 commercially available from Schlumberger	11,8	0

[0080] The results presented in Table 5 indicate that presence of H_3BO_3 and NaOH in the low viscosity fluid increases stability of aggregates.

[0081] *Elevated temperatures*

[0082] Further experiments were conducted on gas containing aggregates at high temperatures (95°C), see FIG. 2A and FIG. 2B In these experiments, agglomerates of guar gel cross-linked by boron containing sand and gas were placed into the glass with tap water. The volumetric ratio of cross-linked gel to clean fluid was 30:70. Composition of aggregates is given in the Table 6.

Table 2: Composition of aggregates.

Guar gum	Typical foaming agent F109	Sand 100 mesh	Nitrogen	Typical borate-based cross-
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	commercially available from Schlumberger			linker J610 commercially available from Schlumberger
25 ppt	1 gpt	5 ppa	Enough to make aggregate buoyant	2 gpt

[0083] FIG. 2A (after 10 minutes) and FIG. 2B (after 30 minutes) are images illustrating the behavior of pillars at 95°C with stabilization additives in the clean fluid (left glass) and without stabilization additives in the clean fluid (left glass). Behavior of pillars was recorded on camera right after placing the experimental beakers into the oven. In the right glass, the clean fluid did not contain any stabilization additives. In the left glass, the low viscosity fluid contained 6gpt of typical borate-based cross-linker J610 commercially available from Schlumberger as a stabilization additive.

[0084] The results shown in FIG. 2A and FIG. 2B indicate that when clean fluid contains stabilization additives it helps the agglomerates to keep their integrity for longer time (left glass) compared to the case when nothing was added to the low viscosity fluid (right glass).

[0085] Further tests were conducted that revealed that even if stabilization additives based on $B(OH)_4^-$ are added to the low viscosity fluid, it did not completely prevent disintegration of the aggregates (unlike in case described in the next example). Thus, the process of aggregate destruction is slowed down.

[0086] Example 4: Stabilisation of guar gel, cross-linked by boron by presence of Zr^{4+} based cross-linker and OH ions in the low viscosity fluid

[0087] In manner similar to that of Example 3, an experiment was conducted with stabilization additives in the clean fluid based on both boron and on Zr^{4+} . A composition of clean fluid was prepared as follows: 525ml of tap water, typical dual cross-linker which contains both borate and zirconate ions, 7.5ml of commercially available J596 from Schlumberger, and NaOH 0.6g as stabilization additives, as also shown in Table 7.

Table 3: Example 4 composition components.

Tap water	Guar gum	Typical foaming agent F109 commercially available from Schlumberger	Sand 100 mesh	Nitrogen	Boric acid solution in water (2 wt.%)	NaOH solution in water (5 wt.%)
225 ml	35 ppt	2 gpt	5 ppa	Enough to make aggregate buoyant	52.8 gpt	2.8 gpt

[0088] In this example, behavior of aggregates containing nitrogen and 5ppa of sand inside clean fluid with dual B^{3+} - Zr^{4+} cross-linkers were tested (the experiment was conducted at 95°C. To test this composition, a bottle which contained both agglomerate and low viscosity fluid with stabilization additives was placed into an oven which had temperature 95°C. The behavior of the pillars was recorded as shown in FIGS. 3A-3C (FIG. 3A-(initially) after 0 minutes; FIG. 3B-after 4 hours; and FIG. 3C-after 7 hours).

[0089] From the experimental results, it can be observed that even after 7 hours the aggregates integrity is maintained at high temperature that was tested. It was also observed that no sand separated out of the agglomerate after the end of experiment.

[0090] Although the preceding description has been described herein with reference to particular means, materials and embodiments, it is not intended to be limited to the particulars disclosed herein; rather, it extends to all functionally equivalent structures, methods and uses, such as are within the scope of the appended claims. Furthermore, although only a few example embodiments have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the example embodiments without materially departing from the disclosure of STABILIZATION OF CROSS-LINKED GELS WITH LOW VISCOSITY FLUIDS DURING DOWNHOLE TREATMENT APPLICATIONS. Accordingly, all such modifications are intended to be included within the scope of this disclosure as defined in the following claims. In the claims, means-plus-function clauses are intended to cover the structures described herein as performing the recited function and not only structural equivalents, but also equivalent structures. Thus, although a nail and a screw may not be structural

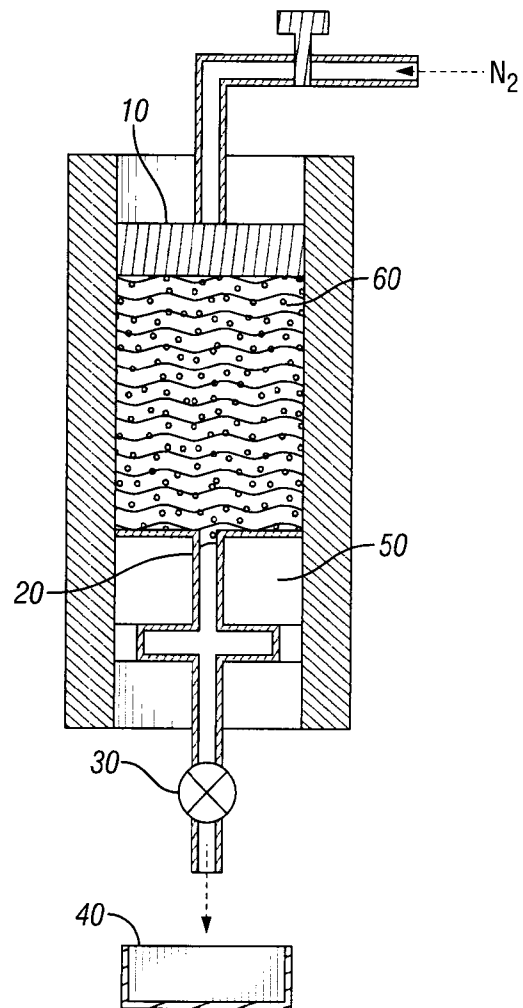
equivalents in that a nail employs a cylindrical surface to secure wooden parts together, whereas a screw employs a helical surface, in the environment of fastening wooden parts, a nail and a screw may be equivalent structures.

WHAT IS CLAIMED IS:

1. A method for treating a subterranean formation comprising:
preparing a treatment fluid including:
a particulate material, and
a polymer gel cross-linked by borate-based cross-linker, wherein the polymeric gel comprises at least one member selected from the group consisting of guar, hydroxypropyl guar and carboxymethylhydroxypropyl guar;
placing the treatment fluid into a subterranean formation via a wellbore; and
placing a low viscosity fluid into the wellbore, the low viscosity fluid comprising stabilization additives in an effective amount to delay or prevent dissolution or dispersion of the polymer gel.
2. The method of claim 1, wherein
an amount of the polymer gel in the treatment fluid is in a range of from about 15 ppt to about 100 ppt, and
an amount of the borate-based cross-linker in the treatment fluid is in a range of from about 0.3 ppt to about 50 ppt.
3. The method of any preceding claim, wherein the treatment fluid and the low viscosity fluid are injected into the wellbore
simultaneously,
by slugs,
by pulses, or
one after another
at a volume ratio of the treatment fluid to the low viscosity fluid that is in a range of from 1:99 to 99:1.
4. The method of any preceding claim, wherein the low viscosity fluid has a viscosity measured at a shear rate 100 s^{-1} and a temperature 25°C from about 1 cP to about 50 cP.
5. The method of preceding claim, wherein the treatment fluid is placed into the subterranean formation during a hydraulic fracturing treatment.
6. The method of any preceding claim, wherein the viscosity of the treatment fluid is in a range that is effective to inhibit settling of the particulate material in the treatment fluid.

7. The method of any preceding claim, wherein the stabilizing additive in one or more member selected from the group consisting of B^{3+} -based cross-linking agents, Ti^{4+} -based cross-linking agents, Zr^{4+} -based cross-linking agents, and pH modifiers.
8. The method of any preceding claim, wherein the treatment fluid further comprises one or more surfactants at an amount in a range of from about 0 to about 20 gpt, and the low viscosity fluid and/or the treatment fluid contain a gas in an amount in a range of from about 0 to about 50 percent by volume of the low viscosity fluid and/or the treatment fluid at downhole conditions.
9. The method of any preceding claim, wherein the low viscosity fluid and/or the polymer gel contain fibers and/or a degradable materials at an amount in a range of from about 0 to about 80 ppt.
10. The method of any preceding claim, wherein the low viscosity fluid further comprises water, slickwater, produced water, brines and/or linear gels.
11. The method of any preceding claim, further comprising initiating syneresis of the polymer gel.
12. The method of any preceding claim, wherein the low viscosity fluid includes borate ion generating chemicals and/or activating ion generating chemicals at a higher concentration than that of the treatment fluid.
13. The method of claims 1-10, wherein the low viscosity fluid includes borate ions generating chemicals and/or activating ion generating chemicals at a lower concentration than that of the treatment fluid.
14. The method of any preceding claim, wherein the low viscosity fluid contains:
 Ti^{4+} -based cross-linking agents and/or Zr^{4+} -based cross-linking agents, and
a concentration of activating ion generating chemicals in the low viscosity fluid is either higher or lower than that of the treatment fluid.
15. The method of any preceding claim, wherein at least a portion of the particulate material is proppant.

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**FIG. 1**

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FIG. 2A



FIG. 2B

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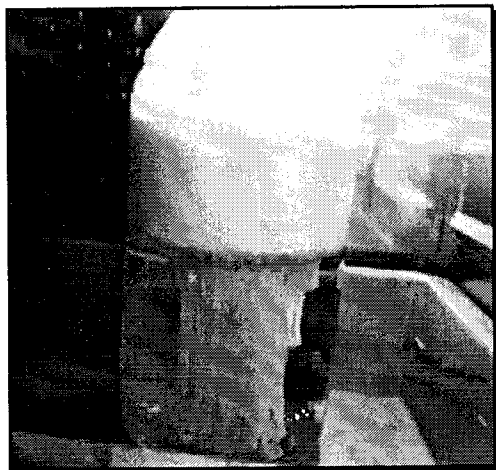


FIG. 3A



FIG. 3B



FIG. 3C

INTERNATIONAL SEARCH REPORT

International application No.

PCT/RU 2015/000272

A. CLASSIFICATION OF SUBJECT MATTER		
E21B 43/267 (2006.01) C09K 8/80 (2006.01) C09K 8/90 (2006.01) 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)		
C09K 8/00-8/94, E21B 43/00-43/27		
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)		
PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, DWPI, EAPATIS, PATENTSCOPE		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2006/0113078 A1 (HALLIBURTON ENERGY SERVICES, INC.) 01.06.2006, claims 1, 10, 39, par. [0021], [0023], [0025], [0035]-[0038], [0064], [0075]	1-3
Y	US 2014/0290943 A1 (SCHLUMBERGER TECHNOLOGY CORPORATION) 02.10.2014, claims 18-20, par. [0032]-[0034], [0066], example 12	1-3
A	US 2013/0213657 A1 (TEXAS UNITED CHEMICAL COMPANY, LLC) 22.08.2013	1-3
A	WO 2001/051767 A2 (SCHLUMBERGER TECHNOLOGY CORPORATION) 19.07.2001	1-3
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents:	"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	
"A" document defining the general state of the art which is not considered to be of particular relevance		
"E" earlier document 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		
Date of the actual completion of the international search	Date of mailing of the international search report	
11 January 2016 (11.01.2016)	11 February 2016 (11.02.2016)	
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37	Authorized officer T. Melnikova Telephone No. 499-240-25-91	

INTERNATIONAL SEARCH REPORT

International application No.

PCT/RU 2015/000272

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-15
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.