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(54) **MULTI-STAGE METHODS AND
COMPOSITIONS FOR DESENSITIZING
SUBTERRANEAN FORMATIONS FACES**

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(57) **ABSTRACT**

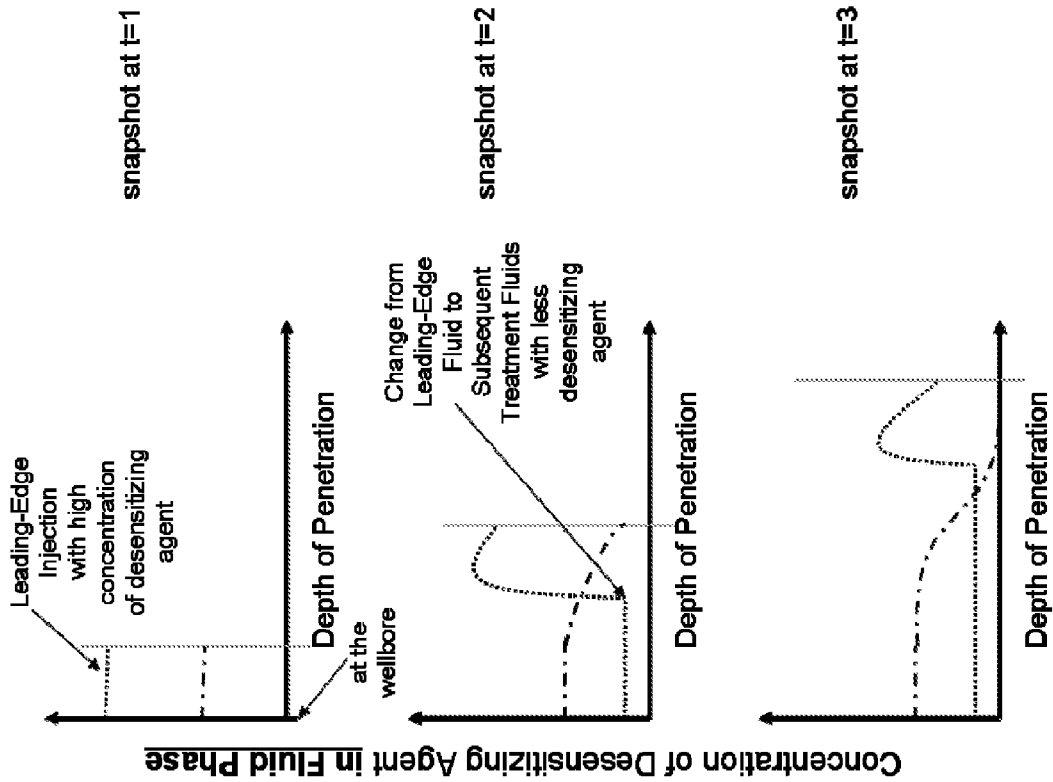
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A method of desensitizing a subterranean formation may include introducing a leading-edge fluid comprising a first base fluid and a first desensitizing agent into at least a portion of the subterranean formation, wherein the first desensitizing agent is present in the first base fluid at a first concentration; and then introducing a treatment fluid comprising a second base fluid and a second desensitizing agent into at least a portion of the subterranean formation, wherein the second desensitizing agent is present in the second base fluid at a second concentration, and wherein the first concentration is higher than the second concentration.

Related U.S. Application Data

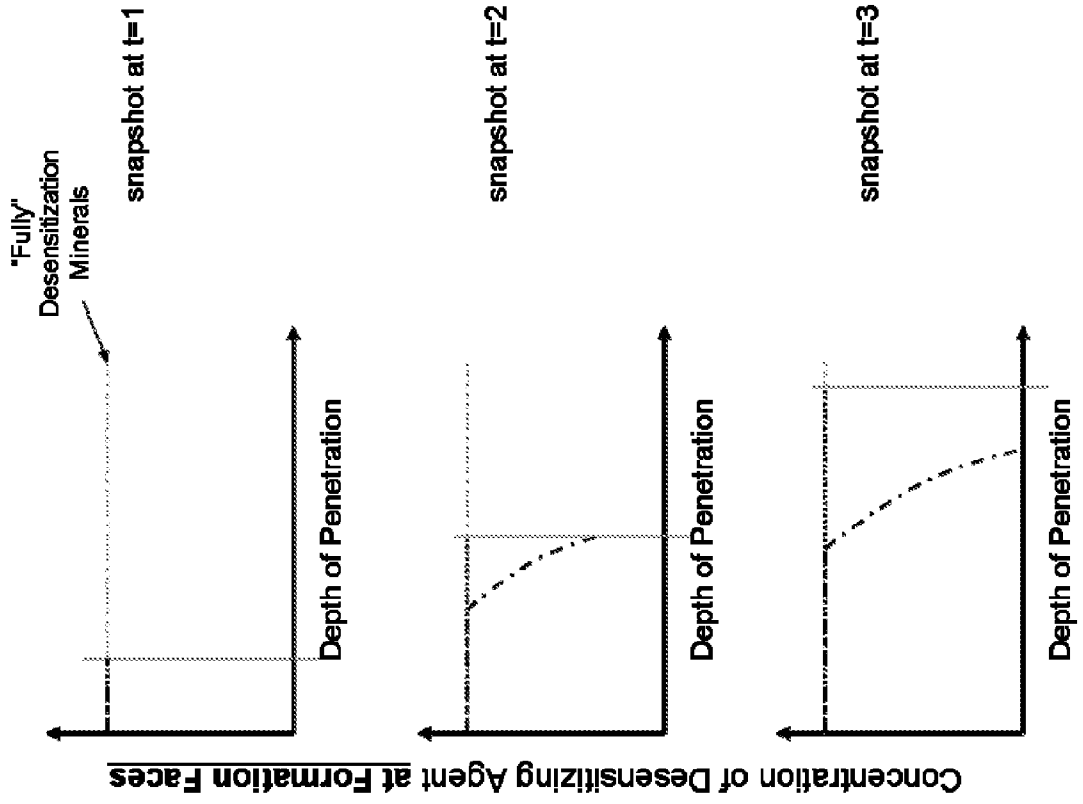
(63) Continuation-in-part of application No. 13/106,382, filed on May 12, 2011.



..... method comprising a leading-edge fluid with subsequent treatment fluids

- - - - - method comprising a constant concentration fluid

Figure 1



..... method comprising a leading-edge fluid with subsequent treatment fluids

- - - - - method comprising a constant concentration fluid

Figure 2

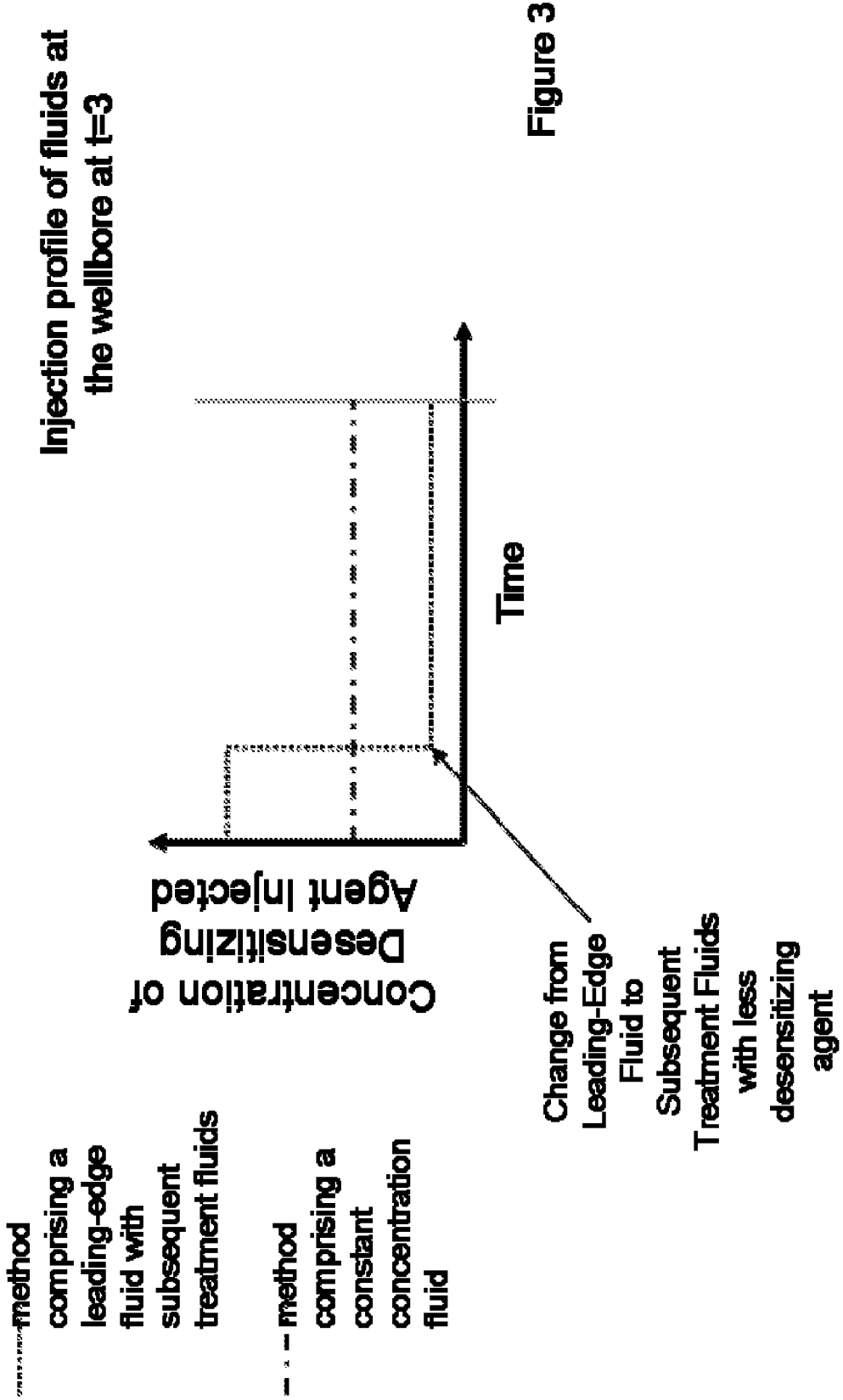


Figure 3

**MULTI-STAGE METHODS AND
COMPOSITIONS FOR DESENSITIZING
SUBTERRANEAN FORMATIONS FACES**

CROSS REFERENCE TO RELATED
APPLICATION

[0001] The present application is a continuation-in-part of U.S. patent application Ser. No. 13/106,382 filed on May 12, 2011, the entire disclosure of which is incorporated herein by reference.

BACKGROUND

[0002] The present invention relates to multi-stage methods for treating a subterranean formation in order to desensitize formation faces to deleterious chemical or physical changes.

[0003] The recovery of fluids such as oil and gas from subterranean formations has been troublesome in formations that contain sensitive minerals capable of undergoing chemical and physical changes along the formation faces, e.g., minerals that swell, slough, degrade, release fines, or become ductile. As used herein, "formation faces" refers to any portion of the formation that is exposed to, for example, a treatment fluid, and includes fracture faces and platelet faces. As used herein, "ductile" refers to becoming able to deform under pressure.

[0004] Often these troublesome formations undergo chemical and physical changes when exposed to aqueous fluids, a common base for subterranean treatment fluids. Troublesome formations may include, but not be limited to, water-sensitive clays, tight gas formations, shales, and coal beds. The terms "clays" and "water-sensitive clays" are used herein interchangeably to generally indicate water-sensitive clays that, when contacted by aqueous fluids in disequilibrium with the minerals in the formation, tend to swell and/or migrate. The clay content of the formations may be a single species of a clay mineral or several species, including, but not limited to, the mixed-layer types of clay. As used herein, the term "tight gas" refers to gas found in sedimentary rock that is cemented together so that permeabilities are relatively low. As used herein, the term "shale" refers to a sedimentary rock formed from the consolidation of fine clay and silt materials into laminated, thin bedding planes. As used herein, "coal bed" refers to a rock formation that may be comprised of, inter alia, one or more types of coal, including, but not limited to, peat, lignite, sub-bituminous coal, bituminous coal, anthracite, and graphite.

[0005] The chemical and physical changes in the formation faces often results in the blockage and/or closure of passage-ways that penetrate the subterranean formation (e.g., fracture network, pore throats, etc.), thereby causing a loss in permeability of the formation. This loss in permeability impairs the flow of fluid through the wellbore and, in some cases, may even completely block the flow of fluids through portions of the formation. Loss in permeability often leads to a decrease in the production for the well. Moreover, some changes in the formation faces, e.g., migrating fines, can be produced with the formation fluids, thereby presenting potential abrasion and other problems with the production equipment and potential reduction in fracture conductivity.

[0006] In an effort to overcome these problems, various methods have been developed for treating problematic formations to desensitize the formation faces from chemical and

physical changes. For example, it has been common practice to add salts to aqueous drilling fluids. The salts adsorb to the clay surfaces in an ion exchange process that can reduce the swelling and/or migration of the clays. Another method used to deter migration is to coat the region with a polymer and/or a consolidating resin in order to physically block the migration of the clays. The term "desensitizing solution" as used herein refers to any solution or suspension used to reduce the sensitivity of minerals within a subterranean formation to chemical and physical changes. The terms "desensitizing components" and "desensitizing agents" as used herein refer to the components of a desensitizing solution that interacts with formation faces to reduce the sensitivity of minerals to chemical and physical changes.

[0007] When a desensitizing solution is exposed to formation faces of problematic formations, the desensitizing agents are removed from the desensitizing solution by the formation faces through known mechanisms including, but not limited to, adsorption, ion exchange, and chemical reaction. As the concentration of the desensitizing agents decreases in the remaining solution, untreated formation faces are exposed to aqueous fluids which promotes the deleterious chemical and physical changes. Current state-of-the-art implementation of desensitizing solutions call for injection of a single bolus of a relatively high concentration of desensitizing solution into the subterranean formation. Using such a method results in the depletion of desensitizing agents most notably at the leading-edge of the desensitizing solution as the solution migrates through the subterranean formation.

SUMMARY OF THE INVENTION

[0008] The present invention relates to multi-stage methods for treating a subterranean formation in order to desensitize formation faces to deleterious chemical or physical changes.

[0009] In some embodiments of the present invention, a method of desensitizing a subterranean formation may comprise: introducing a leading-edge fluid comprising a first base fluid and a first desensitizing agent, wherein the first desensitizing agent is present in the first base fluid at a first concentration; then introducing a treatment fluid comprising a second base fluid and a second desensitizing agent, wherein the second desensitizing agent is present in the second base fluid at a second concentration; and wherein the first concentration is higher than the second concentration.

[0010] In some embodiments of the present invention, a method of desensitizing a subterranean formation may comprise: introducing a leading-edge fluid into a subterranean formation at or above the matrix pressure, wherein the leading-edge fluid comprises a first base fluid and a first desensitizing agent, wherein the first desensitizing agent is present in the first base fluid at a first concentration; then introducing a treatment fluid into the subterranean formation at or above the matrix pressure, wherein the treatment fluid comprises a second base fluid and a second desensitizing agent, wherein the second desensitizing agent is present in the second base fluid at a second concentration; and wherein the first concentration is higher than the second concentration.

[0011] In some embodiments of the present invention, a method of desensitizing a subterranean formation may comprise: introducing a leading-edge fluid comprising a first base fluid and a first desensitizing agent above the matrix pressure into the subterranean formation, wherein the first desensitizing agent is present in the first base fluid at a first concentra-

tion, wherein the first concentration ranges from about 0.1% to about 15% v/v of first desensitizing agent to first base fluid; then introducing a treatment fluid comprising a second base fluid and a second desensitizing agent, wherein the second desensitizing agent is present in the second base fluid at a second concentration, wherein the second concentration ranges from about 0.001% to about 5% v/v of second desensitizing agent to second base fluid; and wherein the desensitizing solution is the same chemical composition in the leading-edge fluid and treatment fluid.

[0012] The features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the preferred embodiments that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The following figures are included to illustrate certain aspects of the present invention, and should not be viewed as exclusive embodiments. The subject matter disclosed is capable of considerable modification, alteration, and equivalents in form and function, as will occur to those skilled in the art and having the benefit of this disclosure.

[0014] FIG. 1 provides illustrative graphs of the concentration of the desensitizing agent within the fluid phase as a function of depth of penetration from the wellbore.

[0015] FIG. 2 provides illustrative graphs of the concentration of the desensitizing agent at the formation faces as a function of depth of penetration from the wellbore.

[0016] FIG. 3 provides an illustrative graph of a nonlimiting example of an injection profile of a wellbore treatment according to the present invention.

DETAILED DESCRIPTION

[0017] The present invention relates to multi-stage methods for treating a subterranean formation in order to desensitize formation faces to deleterious chemical or physical changes.

[0018] Of the many advantages, the present invention provides for methods yielding formation face desensitization, i.e., mineral desensitization, against deleterious chemical and/or physical changes that penetrate deeper into the subterranean formation while decreasing the overall amount of the desensitizing agents. Reduction in the amount of desensitizing agents used can result in a significant cost savings for the operator and may help reduce the environmental impact of the treatment. It should be noted that the term "penetration" refers to both the distance traversed from the wellbore within a fracture network and the radially distance from the fracture into the formation, e.g., penetrating radially several clay platelets deep into the formation along a fracture. It should be noted that the term "formation face" includes the faces encountered radially from the fracture network into the formation.

[0019] In some embodiments, a method of desensitizing a subterranean formation may generally include the steps of: introducing a leading-edge fluid comprising a first base fluid and a first desensitizing agent into at least a portion of the subterranean formation, wherein the first desensitizing agent is present in the first base fluid at a first concentration; and then introducing a treatment fluid comprising a second base fluid and a second desensitizing agent into at least a portion of the subterranean formation, wherein the second desensitizing

agent is present in the second base fluid at a second concentration, and wherein the first concentration is higher than the second concentration.

[0020] Because the leading-edge fluid enters the formation first, it contacts formation faces, such as water-sensitive clays, before other liquids are placed into the formation. That is, the leading-edge fluid is highly likely to encounter sensitive minerals. The depletion of desensitizing agents in the leading-edge fluids, as to contacts new formation faces, may be extensive. Therefore, a high concentration of desensitizing solution in the leading-edge fluid may effectively desensitize minerals as the fluid penetrates the subterranean formation and maintains a desensitizing solution concentration above the necessary amount to desensitize minerals deeper into the subterranean formation. The treatment fluids placed subsequent to the leading-edge fluid may exhibit lower levels of desensitizing solution than required in traditional methods. Because the leading-edge fluid has been placed before the treatment fluid, so long as the interval to be treated by the treatment fluid has been fully contacted by the leading-edge fluid, the treatment fluid needs not act as the primary desensitization fluid. Rather, the desensitizing agents in the treatment fluid following the leading-edge fluid may be used to desensitize any newly exposed minerals during the treatment. Therefore, the concentration of the desensitizing agents in the fracturing fluid is significantly lower than in the leading-edge fluid.

[0021] FIGS. 1-3 compare a nonlimiting example of a treatment according to an embodiment of the present invention to current methods of injecting desensitizing agents at a constant concentration. FIG. 3 illustrates the injection profile, i.e., the concentration injected as a function of time. In this nonlimiting example, the leading-edge method injects first a higher concentration of destabilizing agent than a lower concentration. The method to which this example compares injects a single concentration over the same amount of time. FIGS. 1 and 2 provide a series of illustrative snapshots of what may be occurring over time in the subterranean formation as the two methods would be implemented.

[0022] FIG. 1 looks at the concentration remaining in the fluid phase as a function of depth of penetration into the formation. It should be noted this is meant to illustrate the concentration in solution in the formation, e.g., down the length of a fracture, at a specific time point and not the injection profile. The various time points show the fluid in both treatments being depleted. In the leading-edge fluid method illustrated, the treatment fluid, which has a significantly lower concentration, injected after the leading-edge fluid maintains the level of desensitization and therefore is not significantly depleted. Further illustrated is the level of desensitization of the formation face with a line indicating "fully" desensitized minerals. One skilled in the art, with the benefit of this disclosure, should understand "fully" desensitized minerals includes substantially desensitized and most likely varies based on depth of penetration into the formation. In this example, it is only used to illustrate the point that as desensitizing agents are depleted from the fluid, the leading-edge of the fluid may not have a high enough concentration of desensitizing agents to interact with the formation faces, i.e., sensitive minerals may undergo deleterious chemical and/or physical changes at the leading-edge of a treatment. In some embodiments, the methods of the present invention aim to overcome this problem by introducing a leading-edge fluid

that comprises a higher concentration of desensitizing agents so that at the leading-edge of a treatment sensitive minerals are effectively desensitized.

[0023] Further, FIG. 2 provides the concentration injection profile at time point 3 of FIG. 1. The illustrative method of the present invention uses less desensitizing agent than the method currently implemented. These figures illustrate that the methods provided herein are suited for desensitizing mineral further into a subterranean formation with the need for less overall desensitizing agent.

[0024] The compositions and methods of the present invention may be used in subterranean formations containing water-sensitive clays, tight gas formations, shales, and coal beds. Specifically, subterranean formations may include minerals like, but not limited to, silica; iron minerals; alkaline earth metal carbonates, feldspars, biotite, illite, and chlorite; smectite clays such as montmorillonite, beidellite, nontronite, saponite hectorite and saucanite; kaolin clays such as kaolinite, nacrite, dickite, endellite and halloysite; illite clays such as hydrobiotite, glauconite and illite; chlorite clays such as chlorite, greenalite and chamosite; other clay minerals not belonging to the above groups such as vermiculite, palygorskite, sepiolite; mixed-layer (both regular and irregular) varieties of the above minerals; and any combination thereof.

[0025] Some suitable methods of the present invention may comprise placing a leading-edge fluid comprising a concentrated desensitizing solution into the subterranean reservoir to expose formation faces to the desensitizing agent so as to reduce, or remediate, their sensitivity to deleterious chemical and/or physical changes. Subsequently placed treatment fluids may comprise a lower concentration of desensitizing solution to preserve the existing level of mineral desensitization and/or inhibit sensitization of newly exposed formation faces.

[0026] As used herein, the term "treatment," or "treating," refers to any subterranean operation that uses a fluid in conjunction with a desired function and/or for a desired purpose. The term "treatment," or "treating," does not imply any particular action by the fluid. By way of nonlimiting examples, a treatment fluid introduced into a subterranean formation subsequent to a leading-edge fluid may be a fracturing fluid, an acidizing fluid, a stimulation fluid, a sand control fluid, a completion fluid, a frac-packing fluid, or gravel packing fluid. The methods, leading-edge fluids, and subsequent treatment fluids of the present invention may be used in full-scale operations, pills, or any combination thereof. As used herein, a "pill" is a type of relatively small volume of specially prepared treatment fluid placed or circulated in the wellbore.

[0027] In some embodiments, leading-edge fluids and/or subsequent treatment fluids may be introduced at or above "fracture pressure," which as used herein refers to pressures necessary to create or extend at least one fracture within the subterranean formation. In some embodiments, leading-edge fluids and/or subsequent treatment fluids may be introduced at "matrix pressure," which as used herein refers to pressures below the fracture pressure of the formation.

[0028] In some embodiments, leading-edge fluids may be introduced into a single wellbore multiple times, e.g., multi-stage fracturing operations where sections of the formation are fractured then plugged sequentially where each fracturing includes introducing a leading-edge fluid followed by at least one subsequent treatment fluid.

[0029] In some embodiments, a fracturing method according to the present invention may comprise multiple stages (or sections). The stages may include, but not be limited to,

introducing a leading-edge fluid or a treatment fluid, each with the appropriate concentration of desensitizing agent, that comprise an additive that may include, but not be limited to, proppants; diverting agents including degradable diverting agents; plugs; plugging agents; and any combination thereof. By way of nonlimiting example, a multi-stage treatment may include

[0030] (a) introducing a first leading-edge fluid comprising a first concentration of a desensitizing agent into a first stage of a wellbore penetrating a subterranean formation, the first leading-edge fluid optionally comprising a proppant;

[0031] (b) introducing a first treatment fluid comprising a second concentration of desensitizing agent that is lower than the first concentration into the first stage of the wellbore, the first treatment fluid optionally comprising a proppant;

[0032] (c) introducing a second treatment fluid comprising a diverting agent to substantially divert subsequent fluids from the first stage of the wellbore, the second treatment fluid optionally comprising a desensitizing agent and/or a proppant;

[0033] (d) introducing a second leading-edge fluid comprising a third concentration of a desensitizing agent into a second stage of a wellbore penetrating a subterranean formation, the second leading-edge fluid optionally comprising a proppant;

[0034] (e) introducing a third treatment fluid comprising a fourth concentration of desensitizing agent that is lower than the third concentration into the second stage of the wellbore, the third treatment fluid optionally comprising a proppant;

[0035] (f) introducing a fourth treatment fluid comprising a diverting agent to substantially divert subsequent fluids from the second stage of the wellbore, the fourth treatment fluid optionally comprising a desensitizing agent and/or a proppant; and

[0036] (g) continuing until several stages, e.g., 50 or more, are treated.

[0037] In some embodiments, the stages may be defined by a perforation or a cluster of perforations. It should be noted that the diverting agent in any of the above steps may be interchanged with a plug, e.g., a packer, a bridge plug, a frac plug, or the like, or a plugging agent, e.g., perf balls, gels, plugging foams, degradable diverting agents, and the like. Also, said treatment fluid may be a fracturing fluid. Further, it should be noted that other steps, e.g., flushing treatments and acidizing treatments, may be included within the above non-limiting example. One skilled in the art, with the benefit of this disclosure, should understand the plurality of steps that may be included and the order in which to include them to achieve a desired wellbore treatment design.

[0038] In some embodiments, leading-edge fluids with subsequent treatment fluids may be used in a high-rate water frac including multi-stage high-rate water fracs. These are typically done in shales that have high clay content; therefore, a leading-edge fluid with a desensitizing agent may be especially useful.

[0039] In some embodiments, leading-edge fluids may be used in a remedial treatment for a subterranean formation having at least some formation faces having undergone deleterious chemical and/or physical changes. By way of non-limiting example, a leading-edge fluid may be introduced into a subterranean formation for remediation at a matrix pressure

so as to treat existing formation faces therein. For example, when the fractures are worn out and need to be restimulated.

[0040] In some embodiments, leading-edge fluids with subsequent treatment fluids may be used for injection wells. As used herein, "injection wells" refer to wells in which fluids are injected rather than produced with the primary objective of maintaining reservoir pressure that may assist in production from a nearby well. In formations with sensitive minerals, the deleterious chemical and/or physical changes to formation faces can lead to higher injection pressures needed to maintain reservoir pressure. It is believed that employing leading edge fluids and subsequent treatment fluids, as described in some embodiments herein, could result in a lower injection pressure being required for injection wells.

[0041] In some embodiments, leading-edge fluids with subsequent treatment fluids may be used in a well completion operation, such as a pre-pad fluid in gravel packing operations. The higher concentration of desensitizing agents in a leading-edge fluid would protect the surrounding formation during the wellbore completion operations.

[0042] The optimal concentration of desensitizing agents to use in the leading-edge fluid can be determined by one skilled in the art. One suitable method for determining the optimal concentration of desensitizing agents to be used in the leading-edge fluid involves a four-step analysis. First, determine the total mineral concentration(s) and mineral type (s) from known methods including, but not limited to, x-ray analysis and scanning electron microscopy. Second, determine the desensitizing capacity of a formation sample. By way of non-limiting example, the cation exchange capacity of a formation sample can be determined by Langmuir adsorption isotherms, surface roughness, and cation exchange capacity. Third, estimate the generated surface area during the fracture treatment using known simulation methods. Finally, estimate the mass of desensitizing agents required using the values determined in the first three steps.

[0043] An approximate concentration of desensitizing agents to use in the leading-edge fluid can be determined by one skilled in the arts by generally characterizing the degree to which the mineral(s) in the subterranean formation require desensitization. By way of non-limiting example, water-sensitive clays may be categorized as very water sensitive, moderately water sensitive, or minimally water sensitive. Additionally, one skilled in the arts may be able to estimate the necessary desensitization of the minerals in the subterranean formation based on known characteristics of the formation, nearby wells, and similar formations.

[0044] It should be noted that when "about" is provided at the beginning of a numerical list, "about" modifies each number of the numerical list. It should be noted that in some numerical listings of ranges, some lower limits listed may be greater than some upper limits listed. One skilled in the art will recognize that the selected subset will require the selection of an upper limit in excess of the selected lower limit.

[0045] A preferred method for desensitizing minerals calls for the concentration of the desensitizing agents in the leading-edge fluid to range from a lower limit of about 0.01%, 0.05%, 0.1%, 0.5%, 1%, 2%, 5%, or 10% to an upper limit of about 60%, 50%, 25%, 15%, 10%, or 5% v/v, and wherein the concentration may range from any lower limit to any upper limit and encompass any subset therebetween. Minerals requiring more desensitization may require more concentrated desensitizing solution in the leading-edge fluid relative to the fracturing fluid.

[0046] A preferred method for desensitizing minerals calls for the concentration of the desensitizing agents in subsequent treatment fluids to range from a lower limit of about 0.0001%, 0.001%, 0.01%, 0.1%, or 1% to an upper limit of about 20%, 10%, 5%, 2%, 1%, or 0.1% v/v, where the concentration may range from any lower limit to any upper limit and encompass any subset therebetween. In some embodiments, the concentration of desensitizing agents in the leading-edge fluid may range from a lower limit of about 2, 3, 5, 10, or 25 times to an upper limit of about 5000, 2500, 1000, 500, 100, 75, 50, or 25 times greater than the concentration of desensitizing agents in the treatment fluid, and wherein the concentration may range from any lower limit to any upper limit and encompass any subset therebetween. In some embodiments, the concentration of desensitizing agents may vary during the fracturing operation, i.e., during the introduction of the fracturing fluid. In some embodiments, the concentration change may be step-wise, gradient, or any combination thereof.

[0047] In some embodiments, a transition fluid may be used between the leading-edge fluid and subsequent treatment fluids. The transition fluid may comprise desensitizing agents at an intermediate concentration relative to the leading-edge fluid and subsequent treatment fluids. In some embodiments, a transition fluid may provide for a step-wise, gradient, or combination thereof concentration reduction of the desensitizing agents from the leading-edge fluid to the subsequent treatment fluids. In some embodiments, the transition fluid may be introduced to the subterranean formation at a matrix pressure, at or above formation pressure, or any combination thereof.

[0048] In some embodiments, the concentration of desensitizing agents in leading-edge fluids, transition fluids, and/or subsequent treatment fluids may be adjusted on-the-fly. In some embodiments, the fluid being introduced into the wellbore may be changed based on a pressure change observed at the surface of the wellbore. By way of nonlimiting example, a pressure drop at the surface of a wellbore may indicate fracturing is occurring and a transition to a leading-edge fluid is necessary.

[0049] Nearly all desensitizing agents suitable for use in subterranean operations may be used in the methods of the present invention including, but not limited to, inorganic acids, salts, polyelectrolytes, multivalent ions, inorganic bases, strong bases, oxides, resins, surfactants, polymers, cationic polymers, methyl glucosides, polyglycerols, polyglycols, emulsion facilitating particles, chelating agents, phosphines, soluble organic stabilizing compounds, silica control agents, embrittlement modification agents, surface modification agents, microparticles, nanoparticles, and any combination thereof. The desensitizing agents may be the same or different chemical compositions within the various fluids for use in the methods provided herein. Utilizing different chemical compositions may be advantageous to further reduce costs. By way of nonlimiting example, the leading-edge fluid may comprise an expensive desensitizing agent that is more effective at desensitizing formation faces. Subsequent fluids may be less expensive desensitizing agents that maintain the level of desensitization at the formation faces. Further, the desensitizing agents may be for desensitizing a single mineral composition or multiple mineral compositions, e.g., desensitizing water-swallowable clays and shales in a single treatment fluid. When more than one desensitizing agent is used, the desensitizing agents can be at the same or different concen-

trations relative to one another within the various fluids for use in the methods provided herein. The preparation of a desensitizing solution is expected to be according to a preferred preparation embodiment for the desensitizing solution, which is known by one skilled in the arts. The desensitizing agents may be in various forms: foams, latexes, microemulsions, emulsions, simple solutions, surfactants, nanoparticles, microparticles, degradable particulates, dry form that later breaks up, gelled form, and combinations thereof.

[0050] Examples of suitable desensitizing agents and mechanisms of desensitization may be found in the following documents, all of which are incorporated herein by referenced: U.S. Pat. Nos. 7,740,071; 5,197,544; and 4,366,073, U.S. Patent Publication No. 2004/0235667, and U.S. patent application Ser. Nos. 13/113,533 (filed May 23, 2011 and titled "Silica Control Agents for Use in Subterranean Treatment Fluids"); 12/751,770 (filed May 31, 2010 and titled "Methods for Strengthening Fractures in Subterranean Formations"); 12/826,426 (filed Jun. 29, 2010 and titled "Methods Relating to Improved Stimulation Treatments and Strengthening Fractures in Subterranean Formations"; and 12/851,953 (filed Aug. 6, 2010 and titled "Methods for Strengthening Fractures in Subterranean Formations").

[0051] Desensitizing agents may interact with the surfaces, interlayers, and cores of minerals and mineral platelets to mitigate or reverse mineral hydration, swelling, and sloughing. Charges on the minerals and mineral platelets may permit interaction with dissolved/suspended molecules and ions in fluids, both native and non-native to the formation. The net negative charge on a platelet may be typically balanced mainly by cationic molecules and ions, e.g., sodium ions and silicates. The cations, or charge-balancing ions, associated with the platelet faces are termed "exchangeable" as they can be readily substituted with other cations when presented to the clay platelets. Each macroscopic mineral particle may be comprised of many thousands of sandwiched mineral platelets, each having exchangeable cations and a layer of water therebetween. When the mineral and water are mixed, water may penetrate between the platelets, forcing them further apart. The cations present at the platelet faces may begin to diffuse away from platelet faces. Further, the amount of water contained within the platelets may be dependant upon the pressure under which the mineral is located, typically the depth of the mineral deposit in the subterranean formation. Mechanisms of mineral hydration may include surface hydration through bonding of water molecules to oxygen atoms on the surface of mineral platelets; ionic hydration through hydration of interlayer cations with surrounding shells of water molecules; and osmotic hydration, which occurs in some minerals after they are completely surface hydrated and ionically hydrated, usually at 100% humidity. Suitable desensitizing agents may include, but not be limited to, salts, resins, soluble organic stabilizing compounds, silica control agents, embrittlement modification agents, and any combination thereof.

[0052] Nearly all inorganic acids, organic acids, salts thereof, and combinations thereof known in the art that are suitable for use in subterranean operations may be used in the methods of the present invention including, but not limited to, inorganic acids, salts of inorganic acids, organic acids, salts of organic acids, or any combination thereof. A "salt" of an acid, as that term is used herein, refers to any compound that shares the same base formula as the referenced acid, but one of the hydrogen cations thereon is replaced by a different cation

(e.g., an antimony, bismuth, potassium, sodium, calcium, magnesium, cesium, zinc cation). Suitable inorganic salts may include cations of Group I and II elements. The term "inorganic acid" refers to any acidic compound that does not comprise a carbon atom. Examples of suitable salts of inorganic acids include, but are not limited to, sodium chloride, calcium chloride, potassium chloride, sodium bromide, calcium bromide, potassium bromide, sodium sulfate, calcium sulfate, sodium phosphate, calcium phosphate, sodium nitrate, calcium nitrate, cesium chloride, cesium sulfate, cesium phosphate, cesium nitrate, cesium bromide, potassium sulfate, potassium phosphate, potassium nitrate, zinc chloride, magnesium chloride, magnesium bromide, zinc bromide, and the like. Suitable salts may be Group I and II salts. The term "organic acid" refers to any acidic compound that comprises a carbon atom. Examples of suitable salts of organic acids include, but are not limited to, sodium acetate, sodium formate, calcium acetate, calcium formate, cesium acetate, cesium formate, potassium acetate, potassium formate, magnesium acetate, magnesium formate, zinc acetate, zinc formate, antimony acetate, antimony formate, bismuth acetate, and bismuth formate.

[0053] Suitable inorganic acids may include, but not be limited to, hydrochloric acid, nitric acid, phosphoric acid, sulfuric acid, boric acid, and the like, or any combination thereof. Suitable organic acids may include, but not be limited to, acetic acid, formic acid, citric acid, oxalic acid, and the like, or any combination thereof.

[0054] When included, the various fluids for use in the methods provided herein may comprise any combination of inorganic acids, salts of inorganic acids, organic acids, and/or salts of organic acids. The one or more inorganic acids and/or organic acids (or salts thereof) may be present in the various fluids for use in the methods provided herein in an amount sufficient to provide the desired effect. The amount of the inorganic acid(s) and/or organic acid(s) (or salts thereof) included in the various fluids for use in the methods provided herein may depend upon the particular acid and/or salt thereof used, as well as other components of the various fluids, and/or other factors that will be recognized by one of ordinary skill in the art with the benefit of this disclosure.

[0055] Inorganic bases, organic bases, strong bases, and combinations thereof known in the art suitable for use in subterranean operations may be used in the methods of the present invention. Suitable inorganic bases may include, but not be limited to, sodium hydroxide, ammonium hydroxide, barium hydroxide, calcium hydroxide, magnesium hydroxide, potassium hydroxide, sodium carbonate, ammonium carbonate, barium carbonate, calcium carbonate, magnesium carbonate, potassium carbonate, magnesium chloride triethylamine, sodium amide, and the like, or any combinations thereof. Suitable organic bases may include, but not be limited to, pyridine, methyl amine, imidazole, benzimidazole, histidine, phosphazene, dimethylaniline, trimethylamine, piperidine, and the like, or any combination thereof. Suitable strong bases may include, but not be limited to, sodium hydroxide, potassium hydroxide, calcium hydroxide, barium hydroxide, and the like, or any combination thereof.

[0056] When included, the various fluids for use in the methods provided herein may comprise any combination of inorganic bases, organic bases, and strong bases. The one or more inorganic bases, organic bases, and strong bases may be present in the various fluids for use in the methods provided herein in an amount sufficient to provide the desired effect.

The amount of the inorganic bases, organic bases, and strong bases included in the various fluids for use in the methods provided herein may depend upon the particular base used, as well as other components of the various fluids, and/or other factors that will be recognized by one of ordinary skill in the art with the benefit of this disclosure.

[0057] To the extent they are useful as desensitizing agents, any polymer or resin known in the art that is suitable for use in subterranean operations may be used in the methods of the present invention, including salts thereof. Of these, cationic polymer may be preferred, e.g., amines and imines. The polymers and resins can be synthetic or natural and non-hardenable or hardenable. Polymers and resins suitable for use in the present invention include all polymers, resins, and combinations thereof known in the art that desensitize clay. Examples of polymers and resins suitable for use in the present invention include, but are not limited to: acrylic acid polymers; partially hydrolyzed polyacrylamide (PHA); acrylic acid ester polymers; acrylic acid derivative polymers; acrylic acid homopolymers; acrylic acid ester homopolymers (such as poly(methyl acrylate), poly(butyl acrylate), and poly(2-ethylhexyl acrylate)); acrylic acid ester co-polymers; methacrylic acid derivative polymers; methacrylic acid homopolymers; methacrylic acid ester homopolymers (such as poly(methyl methacrylate), poly(butyl methacrylate), and poly(2-ethylhexyl methacrylate)); acrylamido-methyl-propane sulfonate polymers; acrylamido-methyl-propane sulfonate derivative polymers; acrylamido-methyl-propane sulfonate co-polymers; acrylic acid/acrylamido-methyl-propane sulfonate co-polymers; bisphenol A diglycidyl ether resins; butoxymethyl butyl glycidyl ether resins; bisphenol A-epichlorohydrin resins; bisphenol F resins; polyepoxide resins; novolak resins; polyester resins; phenol-aldehyde resins; urea-aldehyde resins; furan resins; urethane resins; glycidyl ether resins; other epoxide resins; polyacrylamide; partially hydrolyzed polyacrylamide; copolymers of acrylamide and acrylate; carboxylate-containing terpolymers; tetrapolymers of acrylate; galactose; mannose; glucoside; glucose; xylose; arabinose; fructose; glucuronic acid; pyranosyl sulfate; guar gum; locust bean gum; tara; konjak; tamarind; starch; cellulose; karaya; xanthan; tragacanth; carrageenan; polycarboxylates such as polyacrylates and polymethacrylates; polyacrylamides; methylvinyl ether polymers; polyvinyl alcohols; polyvinylpyrrolidone; polyalkylene imines (such as polyethylene imine and polypropylene imine); polyamines (such as putrescine, cadaverine, spermidine, spermine, diethylenetriamine, tetramethylenediamine, trimethylenetetramine, tetraethylenepentamine, polyethylene amine, cyclen); organo-polyamines; quaternized polyamines; CLA-STA® XP (a water-soluble cationic oligomer, available from Halliburton Energy Services, Inc.); CLA-STA® FS (a mineral stabilizing polymer, available from Halliburton Energy Services, Inc.); and CLA-WEB™ (a stabilizing additive, available from Halliburton Energy Services, Inc); derivatives thereof; salts thereof; and combinations thereof.

[0058] The polymers or resins (or salts thereof) and combinations thereof may be present in the various fluids for use in the methods provided herein in an amount sufficient to provide the desired effect. The amount of the polymer or resin (or salts thereof) included in the various fluids for use in the methods provided herein may depend upon the particular polymer, resin, and/or salt thereof used, as well as other

components of the various fluids, and/or other factors that will be recognized by one of ordinary skill in the art with the benefit of this disclosure.

[0059] Suitable surfactants and combinations thereof for use in the present invention may include anionic surfactants, cationic surfactants, amphoteric surfactants, and/or nonionic surfactants. Examples of surfactants that may be suitable for use in the present invention include, but are not limited to C₁₂ to C₂₂ alkyl phosphonate surfactants, ethoxylated nonyl phenol phosphate esters, ethoxylated fatty acids, sodium dodecyl sulfate, poly(vinyl alcohol), sodium dodecylbenzenesulfonic acid, cetyltrimethylammonium bromide, cetylpyridinium bromide, hexadecylmaltoside, trimethylcocoammonium chloride, trimethyltallowammonium chloride, dimethyldicoammonium chloride, bis(2-hydroxyethyl)tallowamine, bis(2-hydroxyethyl)erucylamine, erucyl methyl bis(2-hydroxyethyl)ammonium chloride, bis(2-hydroxyethyl)coco-amine, cetylpyridinium chloride, N,N,N-trimethyl-1-octadecammonium chloride, fatty amine salts, polyamines, ammonium salts, quaternary ammonium compounds (e.g., alkyl quaternary ammonium salts), alkyl pyridinium salts, and any derivatives thereof. An example of commercially-available surfactants that may be suitable in certain embodiments of the present invention is 19N™ surfactant (a cationic nonemulsifier, available from Halliburton Energy Services, Inc.), TWEEN® surfactants (a polysorbate surfactant, available from Sigma-Aldrich), TRITON® surfactants (a nonionic surfactant, available from Sigma-Aldrich), and BRIJ® surfactants (a nonionic surfactant, available from Sigma-Aldrich). Certain cationic surfactants may be incompatible or undesirable to use with certain anionic polymers, minerals present on the mineral surface, and/or other elements or conditions in a treatment fluid (e.g., pH) and/or subterranean formation present in a particular application of the present invention. One of skill in the art, with the benefit of this disclosure, should be able to select a cationic surfactant that is compatible with these elements.

[0060] The surfactants (or salts thereof) and combinations thereof may be present in the various fluids for use in the methods provided herein in an amount sufficient to provide the desired effect. The amount of the surfactant (or salts thereof) included in the various fluids for use in the methods provided herein may depend upon the particular surfactant and/or salt thereof used, as well as other components of the various fluids, and/or other factors that will be recognized by one of ordinary skill in the art with the benefit of this disclosure.

[0061] In some embodiments, particulates may comprise emulsion facilitating particles, i.e., any particle with a size smaller than a discontinuous phase droplet in the emulsion. In some exemplary embodiments, the emulsion facilitating particles have a size less than about 75 microns. Generally, smaller emulsion facilitating particles are preferred. Suitable examples of emulsion facilitating particles include particles that have or exhibit a suitable fluid contact angle, such as any organically modified material, metal sulfate, or polymer. Suitable organically modified materials may include modified silicas, modified fumed silicas, or various clay types. Fumed silicas may have slightly different degrees of organic modification when small amounts of dimethyldichlorosilane are added in the process of fuming the silica. Examples of suitable modified silicas or modified fumed silicas include, but not be limited to, HDK® silicas (silica silylates, Wacker-Chemie GmbH) such as HDK® H20, HDK® H30, and

HDK® H2000. The HDK® silicas are loose white powders that are primarily amorphous lattice structures of SiO₂. Suitable organically modified materials also may include organically modified aluminum, titanium, zirconium, or various clay types. Various clay types may include non-kaolinitic clays such as bentonite, kaolin clays, and any other clay types capable of cation exchange.

[0062] The emulsion facilitating particles and combinations thereof may be present in the various fluids for use in the methods provided herein in an amount sufficient to provide the desired effect. The amount of the emulsion facilitating particles included in the various fluids for use in the methods provided herein may depend upon the particular emulsion facilitating particles used, as well as other components of the various fluids, and/or other factors that will be recognized by one of ordinary skill in the art with the benefit of this disclosure.

[0063] Nearly all organic stabilizing compounds and combinations thereof known in the art that are suitable for use in subterranean operations may be used in the methods of the present invention.

[0064] Examples of suitable organic acids include, but are not limited to, formic acid, acetic acid, citric acid, glycolic acid, lactic acid, 3-hydroxypropionic acid, a C₁ to C₁₂ carboxylic acid, an aminopolycarboxylic acid such as hydroxyethylethylenediamine triacetic acid, and combinations thereof. Alternatively or in combination with the one or more organic acids, the various fluids for use in the methods provided herein may comprise a salt of an organic acid. A "salt" of an acid, as that term is used herein, refers to any compound that shares the same base formula as the referenced acid, but one of the hydrogen cations thereon is replaced by a different cation (e.g., an antimony, bismuth, potassium, sodium, calcium, magnesium, cesium, or zinc cation). Examples of suitable salts of organic acids include, but are not limited to, sodium acetate, sodium formate, calcium acetate, calcium formate, cesium acetate, cesium formate, potassium acetate, potassium formate, magnesium acetate, magnesium formate, zinc acetate, zinc formate, antimony acetate, antimony formate, bismuth acetate, and bismuth formate. The one or more organic acids (or salts thereof) may be present in the various fluids for use in the methods provided herein in an amount sufficient to provide the desired effect. The amount of the organic acid(s) (or salts thereof) included in the various fluids for use in the methods provided herein may depend upon the particular acid and/or salt used, as well as other components of the treatment fluid, and/or other factors that will be recognized by one of ordinary skill in the art with the benefit of this disclosure.

[0065] A variety of monomers (or salts thereof) are suitable for use as an organic stabilizing compound in the present invention. Examples of suitable monomers include, but are not limited to, acrylic acid, methacrylic acid, acrylamide, methacrylamide, 2-methacrylamido-2-methylpropane sulfonic acid, dimethylacrylamide, vinyl sulfonic acid, N,N-dimethylaminoethylmethacrylate, 2-triethylammoniumethylmethacrylate chloride, N,N-dimethylaminopropylmethacrylamide, methacrylamidepropyltriethylammonium chloride, N-vinyl pyrrolidone, quaternary amines, imidazolium salts, phosphonium salts, vinyl-phosphonic acid, methacryloyloxyethyl trimethylammonium sulfate, 1-carboxy-N,N,N-trimethylmethanaminium chloride, 2-hydroxy-N,N,N-trimethyl ethanaminium acetate, 2-hydroxy-N,N,N-trimethyl 1-propan-

aminium acetate, tetra alkyl ammonium, bis-(hydrogenated tallow)-dimethyl-ammonium chloride, bis-(hydrogenated tallow)-benzyl-methyl-ammonium chloride, 4,5-dihydro-1-methyl-2-nortallow-alkyl-1-(2-tallow-amidoethyl)-imidazolium methyl sulfate, 1-ethyl-4,5-dihydro-3-(2-hydroxyethyl)-2-(8-heptadecenyl)-imidazolium ethyl sulfate, putrescine, cadaverine, spermidine, spermine, diethylenetriamine, tetramethylenediamine, trimethylenetetramine, tetraethylenepentamine, and any combination thereof.

[0066] The organic stabilizing compounds and combinations thereof may be present in the various fluids for use in the methods provided herein in an amount sufficient to provide the desired effect. The amount of the organic stabilizing compounds included in the various fluids for use in the methods provided herein may depend upon the particular organic stabilizing compounds used, as well as other components of the various fluids, and/or other factors that will be recognized by one of ordinary skill in the art with the benefit of this disclosure.

[0067] Nearly all chelating agents and combinations thereof known in the art that are suitable for use in subterranean operations may be used in the methods of the present invention. Suitable chelating agents may comprise amines, esters, carboxylic acids, alcohols, ethers, aldehydes, ketones, mercaptans, thiols, and/or combinations thereof. Examples of suitable chelating agents include ethylenediaminetetraacetic acid ("EDTA"), nitrilotriacetic acid ("NTA"), hydroxyethylethylenediaminetriacetic acid ("HEDTA"), dicarboxymethyl glutamic acid tetrasodium salt ("GLDA"), diethylenetriaminepentaacetic acid ("DTPA"), propylenediaminetetraacetic acid ("PDTA"), ethylenediaminedi(o-hydroxyphenylacetic) acid ("EDDHA"), glucoheptonic acid, gluconic acid, amino tri(methylene phosphonic acid), penta sodium salt of aminotri(methylene phosphonic acid), tetra sodium salt of aminotri(methylene phosphonic acid), 1-hydroxyethylidene-1,1,-diphosphonic acid, hexamethylenediamine tetra(methylene phosphonic acid), diethylenetriamine penta(methylene phosphonic acid), bis(hexamethylene triamine penta(methylene phosphonic acid)), 2-phosphonobutane-1,2,4-tricarboxylic acid, monoethanolamine diphosphonate, etidronic acid, potassium salts of (1-hydroxyethylidene) diphosphonic acid, tetrasodium (1-hydroxyethylidene) biphosphonate, sodium salts of (1-hydroxyethylidene) diphosphonic acid, disodium salts of hydroxyethylidene 1,1-diphosphonic acid, sodium salts of diethylene triamine penta(methylene phosphonic acid), sodium salts of bis hexamethylene triamine penta(methylene phosphonic acid), sodium salts of 2-phosphonobutane-1,2,4-tricarboxylic acid, tetrasodium etidronate, maleic acid, polymers of modified polyacrylic acid, sulphonated polyacrylic acid, carboxymethyl inulin, any salt thereof, any derivative thereof, and any combination thereof.

[0068] The chelating agents and combinations thereof may be present in the various fluids for use in the methods provided herein in an amount sufficient to provide the desired effect. The amount of the chelating agents included in the various fluids for use in the methods provided herein may depend upon the particular chelating agents used, as well as other components of the various fluids, and/or other factors that will be recognized by one of ordinary skill in the art with the benefit of this disclosure.

[0069] Nearly all silica control agents and combinations thereof known in the art that are suitable for use in subterranean operations may be used in the methods of the present

invention. Without limiting the invention to a particular theory or mechanism of action, it is nevertheless currently believed that silica may act as a binder of clay, sand, diagenetic minerals, clasts, and/or other fine particulates in subterranean formations.

[0070] In some embodiments, the silica control agent may comprise a compound chosen from the group consisting of: silica, silicates (e.g., orthosilicates, pyrosilicates, cyclic-silicates, single chain silicates, double chain silicates, sheet silicates, colloidal silicates), silanes, organo-silanes, and any combination thereof. In some embodiments, the silica control agent may be provided by a natural mineral comprising silica or a silicate. Suitable examples of naturally occurring minerals comprising silica or a silicate include, but are not limited to, phenacite, willemitite, zircon, olivine, garnet, thortveitite, benitoite, beryl, pyroxenes, enstatite, spodumene, pollucite, tremolite, crocidolite, talc, petalite, cristobalite, and any combination thereof. One skilled in the art will recognize that in order to be able to use naturally occurring silicates they would need to be finely ground in order to be sufficiently soluble/suspendable. As used herein, the term "finely ground" refers to mesh sizes smaller than or equal to 270 U.S. Mesh (53 microns), 325 U.S. Mesh (44 microns), 400 U.S. Mesh (37 microns), 550 U.S. Mesh (25 microns), 800 U.S. Mesh (15 microns), or 1250 U.S. Mesh (10 microns). Other suitable silicates include, but are not limited to, potassium silicate, calcium silicate, sodium aluminum silicate, and sodium silicate. Suitable commercially available silica control agents may include INJECTROL® (a sealant, available from Halliburton Energy Services, Inc). However, dilution to near the saturation point may be required for such products to be suitable silica control agents in order to avoid precipitation and plugging of the formation. In some preferred embodiments non-polymeric metal silicates, such as sodium silicate or potassium silicate, may be preferred. In some preferred embodiments, the silicate may be sodium silicate having a weight ratio of SiO₂ to Na₂O ranging from about 3.25:1 to 1.5:1. In some preferred embodiments, the silicate may be potassium silicate having a ratio of SiO₂ to K₂O ranging from about 2.5:1 to 1.5:1.

[0071] Silanes may include chemicals that contain silicone at the center of the silane molecule that is chemically attached to a first functional group such as vinyl, amino, chloro, epoxy, mercapto, and a second functional group such as methoxy or ethoxy. Examples of suitable silanes and organo-silanes may include, but not be limited to, N2-(aminoethyl)-3-aminopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, n-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane, methyltrimethoxysilane, vinyltrimethoxysilane, methyltriethoxysilane, tetraethoxysilane, methyltriacetoxysilane, methyl tris-(N-methylbenzamidosisilane), methyl tris-(methyl ethyl ketoximino)silane, methyl tris-(methyl isobutylketoximino)silane, methyl vinyl bis-(methyl ethylketoximino)silane, tetrakis-(methyl ethylketoximino)silane, methyl tris-(isprenoxy)silane, methyl tris-(cyclohexylamino)silane, gamma-aminopropyltriethoxysilane, N-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilanes, aminoethyl-N-beta-(aminoethyl)-gamma-aminopropyl-trimethoxysilanes, gamma-ureidopropyl-triethoxysilanes, beta-(3-4 epoxy-cyclohexyl)-ethyl-trimethoxysilane, gamma-glycidoxypropyl-trimethoxysilanes, vinyltrichlorosilane, vinyltris(beta-methoxyethoxy)silane, vinyltriethoxysilane, vinyltrimethoxysilane, 3-metacryloxypropyltrimethoxysilane, beta-(3,4 epoxycyclohexyl)-ethyltrimethoxysilane,

r-glycidoxypropyltrimethoxysilane, r-glycidoxypropylmethyltriethoxysilane, N-B(aminoethyl)-raminopropyl-trimethoxysilane, N-beta(aminoethyl)-raminopropylmethyldimethoxysilane, 3-aminopropyl-triethoxysilane, N-phenyl-r-aminopropyltrimethoxysilane, r-mercaptopropyl-trimethoxysilane, vinyltrichlorosilane, vinyltris(beta-methoxyethoxy)silane, vinyltrimethoxysilane, r-metacryloxypropyl-trimethoxysilane, beta-(3,4 epoxycyclohexyl)-ethyltrimethoxysilane, r-glycidoxypropyltrimethoxysilane, r-glycidoxypropylmethyltriethoxysilane, N-beta(aminoethyl)-r-aminopropyltrimethoxysilane, N-beta(aminoethyl)-r-aminopropylmethyldimethoxysilane, r-aminopropyltriethoxysilane, N-phenyl-raminopropyltrimethoxysilane, r-mercaptopropyltrimethoxysilane, and any derivative thereof, and any combination thereof.

[0072] The silica control agents and combinations thereof may be present in the various fluids for use in the methods provided herein in an amount sufficient to provide the desired effect. The amount of the silica control agents included in the various fluids for use in the methods provided herein may depend upon the particular silica control agent used, as well as other components of the various fluids, and/or other factors that will be recognized by one of ordinary skill in the art with the benefit of this disclosure.

[0073] Nearly all embrittlement modification agents and combinations thereof known in the art that are suitable for use in subterranean operations may be used in the methods of the present invention. The term "embrittlement" and its derivatives as used herein refers to a process by which the properties of a material are changed through a chemical interaction such that a material that originally behaves in a ductile or plastic manner is transformed to a material that behaves in a more brittle manner. This may be determined by examining the Young's modulus and the Poisson's ratio of the natural rock before treatment. If the rock has become embrittled, the Young's modulus should be higher and the Poisson's ratio should be lower as compared to the natural rock before treatment.

[0074] Young's modulus is the ratio of stress, which has units of pressure, to strain, which is dimensionless; therefore Young's modulus itself has units of pressure. The SI unit of modulus of elasticity (E, or less commonly Y) is the pascal (Pa or N/m²); the practical units are megapascals (MPa or N/mm²) or gigapascals (GPa or kN/mm²). In United States customary units, it is expressed as pounds (force) per square inch (psi). Young's modulus, E, can be calculated by dividing the tensile stress by the tensile strain:

$$E = \frac{\text{tensile stress}}{\text{tensile strain}} = \frac{\sigma}{\epsilon} = \frac{F/A_0}{\Delta L/L_0} = \frac{FL_0}{A_0\Delta L} \quad \text{Equation 1}$$

[0075] Where:

[0076] E is the Young's modulus (modulus of elasticity);

[0077] F is the force applied to the object;

[0078] A₀ is the original cross-sectional area through which the force is applied;

[0079] ΔL is the amount by which the length of the object changes; and

[0080] L₀ is the original length of the object.

[0081] Poisson's ratio (ν) is the ratio, when a sample object is stretched, of the contraction or transverse strain (perpendicular to the applied load), to the extension or axial strain (in the direction of the applied load).

$$\nu = -\frac{\epsilon_{trans}}{\epsilon_{axial}} = -\frac{\epsilon_x}{\epsilon_y} \quad \text{Equation 2}$$

[0082] Where:

[0083] ν is the resulting Poisson's ratio,

[0084] ϵ_{trans} is transverse strain (negative for axial tension, positive for axial compression); and

[0085] ϵ_{axial} is axial strain (positive for axial tension, negative for axial compression).

[0086] Suitable embrittlement modification agents for use in the present invention may comprise high alkaline materials. Suitable examples may include, but not be limited to, lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, cesium hydroxide, sodium carbonate, sodium silicate, lime, amines, ammonia, borates, Lewis bases, other strong bases, and any derivative or combination thereof. The concentration of the embrittlement modification agent in a treatment fluid may depend on the desired pH (e.g., about 10 or above at downhole conditions) of the fluid given the factors involved in the treatment.

[0087] The embrittlement modification agents and combinations thereof may be present in the various fluids for use in the methods provided herein in an amount sufficient to provide the desired effect. The amount of the embrittlement modification agents included in the various fluids for use in the methods provided herein may depend upon the particular embrittlement modification agent used, as well as other components of the treatment fluid, and/or other factors that will be recognized by one of ordinary skill in the art with the benefit of this disclosure.

[0088] Optionally, embrittlement modification agents for use in the present invention may comprise cationic additives, such as cationic polymers and cationic additives, to enhance the plasticity modification. Divalent cationic additives may be more stable. If used, such cationic additives may be used in an amount of about 0.01% to about 1% by weight of the embrittlement modification agents. Hydroxy aluminum and zirconium oxychloride are examples. Other examples may include, but not be limited to, CLA-STA® XP, CLA-STA® FS, CLAYFIX® (an acid salt, available from Halliburton Energy Services, Inc.), CLAYFIX®-II (a temporary clay stabilizing additive, available from Halliburton Energy Services, Inc.), and CLAYFIX®-II PLUS (a temporary clay stabilizing additive, available from Halliburton Energy Services, Inc.), HPT-1™ (a cationic polymer, available from Halliburton Energy Services, Inc.), and combinations thereof. Suitable additives are described in the following patents, each of which are hereby incorporated by reference, U.S. Pat. Nos. 5,097,094, 4,974,678, 4,424,076, and 4,366,071.

[0089] Optionally, embrittlement modification agents for use in the present invention may comprise salt(s) such as salts of lithium, sodium, potassium, rubidium, calcium, strontium, barium, cesium, magnesium, and manganese. The ion exchange resulting from the presence of the salt is useful in aiding in the shrinkage of the rock.

[0090] Optionally, including surfactants in the embrittlement modification agents may facilitate ultra low surface tensions and allow these fluids to penetrate into a subterranean formation more easily, e.g., via microfractures and between mineral platelets.

[0091] The term "microparticles" as used herein refers to particles less than 500 microns in one dimension, but larger than nanoparticles. The term "nanoparticles" as used herein refers to particles with at least one dimension less than about 100 nm.

[0092] Nearly all microparticles and combinations thereof known in the art that are suitable for use in subterranean operations and can adsorb and/or bind to minerals may be used in the methods of the present invention. Examples of suitable microparticles may include, but not be limited to, metal oxide microparticles like silica, titania, alumina, magnesium oxide, calcium oxide, and the like; minerals like slag, zeolite, vitrified shale, silica flour, silica sand; polymeric microparticles including those that comprise the polymers and/or resins disclosed herein; or any combination thereof.

[0093] Nearly all nanoparticles and combinations thereof known in the art that are suitable for use in subterranean operations and can adsorb and/or bind to minerals may be used in the methods of the present invention. Examples of suitable nanoparticles may include, but not be limited to, carbon nanoparticles like fullerenes (spherical or otherwise), endofullerenes, nanotubes (single or multi-walled), filled nanotubes, carbon nanohorns, carbon nano-bamboo, graphene (single to few layer thick), and carbon quantum dots; metal oxide nanoparticles like silica, titania, alumina, iron oxide, manganese oxide, zinc oxide, molybdenum oxide, magnesium oxide, and calcium oxide; metal nanoparticles like gold, palladium, silver, and palladium; nitride nanoparticles; carbide nanoparticles; magnetic nanoparticles like Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$; quantum dots like CdSe and ZnS; any derivative thereof; and any combination thereof. It should be noted that nanoparticles include nanorods, nanospheres, nanorices, nanowires, nanostars (like nanotripods and nanotetrapods), hollow nanostructures, hybrid nanostructures that are two or more nanoparticles connected as one, and non-nano particles with nano-coatings or nano-thick walls. It should be further noted that nanoparticles include the functionalized derivatives of nanoparticles including, but not limited to, nanoparticles that have been functionalized covalently and/or non-covalently, e.g., pi-stacking, physisorption, ionic association, van der Waals association, and the like. Suitable functional groups may include, but not be limited to, moieties comprising amines (1° , 2° , or 3°), amides, carboxylic acids, aldehydes, ketones, ethers, esters, peroxides, silyls, organosilanes, hydrocarbons, aromatic hydrocarbons, and any combination thereof; polymers; chelating agents like ethylenediamine tetraacetate, diethylenetriaminepentaacetic acid, triglycollamic acid, and a structure comprising a pyrrole ring; and any combination thereof.

[0094] As described above, the various fluids described herein may comprise proppants. Proppants suitable for use in the present invention may comprise any material suitable for use in subterranean operations. Suitable materials for these proppants include, but are not limited to, sand, bauxite, ceramic materials, glass materials, polymer materials, polytetrafluoroethylene materials, nut shell pieces, cured resinous particulates comprising nut shell pieces, seed shell pieces, cured resinous particulates comprising seed shell pieces, fruit pit pieces, cured resinous particulates comprising fruit pit pieces, wood, composite particulates, and combinations thereof. Suitable composite particulates may comprise a binder and a filler material wherein suitable filler materials include silica, alumina, fumed carbon, carbon black, graphite, mica, titanium dioxide, meta-silicate, calcium silicate,

kaolin, talc, zirconia, boron, fly ash, hollow glass microspheres, solid glass, and combinations thereof. The mean particulate size generally may range from about 2 mesh to about 400 mesh on the U.S. Sieve Series; however, in certain circumstances, other mean particulate sizes may be desired and will be entirely suitable for practice of the present invention. In particular embodiments, preferred mean particulates size distribution ranges are one or more of 6/12, 8/16, 12/20, 16/30, 20/40, 30/50, 40/60, 40/70, or 50/70 mesh. It should be understood that the term "particulate," as used in this disclosure, includes all known shapes of materials, including substantially spherical materials, fibrous materials, polygonal materials (such as cubic materials), and combinations thereof. Moreover, fibrous materials, that may or may not be used to bear the pressure of a closed fracture, may be included in certain embodiments of the present invention. In certain embodiments, the proppant may be present in the various fluids described herein in an amount in the range of from about 0.5 pounds per gallon ("ppg") to about 30 ppg by volume of the treatment fluid, and encompass any subset therebetween.

[0095] The base fluid of a leading-edge fluid, transition fluid, and/or treatment fluid may comprise oil-based fluids, aqueous-based fluids, aqueous-miscible fluids, water-in-oil emulsions, or oil-in-water emulsions. Suitable oil-based fluids may include alkanes, olefins, aromatic organic compounds, cyclic alkanes, paraffins, diesel fluids, mineral oils, desulfurized hydrogenated kerosenes, and any combination thereof.

[0096] Suitable aqueous-based fluids may include fresh water, saltwater (e.g., water containing one or more salts dissolved therein), brine (e.g., saturated salt water), seawater, and any combination thereof. Generally, the water may be from any source, provided that it does not contain components that might adversely affect the stability and/or performance of the leading-edge fluid or the fracturing fluid of the present invention. In certain embodiments, the density of the aqueous base fluid can be adjusted, among other purposes, to provide additional particulate transport and suspension in the leading-edge fluid or the fracturing fluid used in the methods of the present invention. In certain embodiments, the pH of the aqueous base fluid may be adjusted (e.g., by a buffer or other pH adjusting agent), among other purposes, to reduce the viscosity of the leading-edge fluid or fracturing fluid. In these embodiments, the pH may be adjusted to a specific level, which may depend on, among other factors, the types of gelling agents, acids, and other additives included in the leading-edge fluid or fracturing fluid. One of ordinary skill in the art, with the benefit of this disclosure, will recognize when such density and/or pH adjustments are appropriate.

[0097] Suitable aqueous-miscible fluids may include, but not be limited to, alcohols, e.g., methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, isobutanol, and t-butanol; glycerins; glycols, e.g., polyglycols, propylene glycol, and ethylene glycol; polyglycol amines; polyols; any derivative thereof; any in combination with salts, e.g., sodium chloride, calcium chloride, calcium bromide, zinc bromide, potassium carbonate, sodium formate, potassium formate, cesium formate, sodium acetate, potassium acetate, calcium acetate, ammonium acetate, ammonium chloride, ammonium bromide, sodium nitrate, potassium nitrate, ammonium nitrate, ammonium sulfate, calcium nitrate, sodium carbonate, and potassium carbonate; any in combination with an aqueous-based fluid; and any combination thereof.

[0098] Suitable water-in-oil emulsions, also known as invert emulsions, may have an oil-to-water ratio from a lower limit of greater than about 50:50, 55:45, 60:40, 65:35, 70:30, 75:25, or 80:20 to an upper limit of less than about 100:0, 95:5, 90:10, 85:15, 80:20, 75:25, 70:30, or 65:35 by volume in the base treatment fluid, and wherein the amount may range from any lower limit to any upper limit and encompass any subset therebetween. Examples of suitable invert emulsions include those disclosed in U.S. Pat. No. 5,905,061, U.S. Pat. No. 5,977,031, and U.S. Pat. No. 6,828,279, each of which are incorporated herein by reference. It should be noted that for water-in-oil and oil-in-water emulsions, any mixture of the above may be used including the water being an aqueous-miscible fluid.

[0099] In some embodiments, the base fluid may be foamed, i.e., may comprise a foaming agent and a gas. Suitable foaming agents may be any known foaming agent that does not cause deleterious chemical and/or physical changes to the formation faces and may be used in a sufficient amount to achieve a desired foam, which should be known to one skilled in the art. In some embodiments, the gas is selected from the group consisting of nitrogen, carbon dioxide, air, methane, helium, argon, and any combination thereof. In some embodiments, the quality of the foamed fracturing fluid may range from a lower limit of about 5%, 10%, 25%, 40%, 50%, 60%, or 70% gas volume to an upper limit of about 99%, 90%, 80%, 75%, 60%, or 50% gas volume, and wherein the quality of the foamed fracturing fluid may range from any lower limit to any upper limit and encompass any subset therebetween.

[0100] The various fluids described herein can further comprise additives including, but not limited to, salts, weighting agents, inert solids, fluid loss control agents, emulsifiers, dispersion aids, corrosion inhibitors, emulsion thinners, emulsion thickeners, viscosifying agents, high-pressure and high-temperature emulsifier-filtration control agents, surfactants, particulates, proppants, lost circulation materials, foaming agents, gases, pH control additives, breakers, biocides, crosslinkers, stabilizers, scale inhibitors, mutual solvents, oxidizers, reducers, friction reducers, and any combination thereof.

[0101] In some embodiments, a method of desensitizing a subterranean formation may generally include the steps of: introducing a leading-edge fluid comprising a first base fluid and a first desensitizing agent into at least a portion of the subterranean formation, wherein the first desensitizing agent is present in the first base fluid at a first concentration; and then introducing a treatment fluid comprising a second base fluid and a second desensitizing agent into at least a portion of the subterranean formation, wherein the second desensitizing agent is present in the second base fluid at a second concentration, and wherein the first concentration is higher than the second concentration.

[0102] In some embodiments, a method of remedially desensitizing a subterranean formation may generally include the steps of: providing a wellbore penetrating a subterranean formation that comprises a plurality of formation faces, the formation faces having undergone deleterious chemical and/or physical changes; introducing a leading-edge fluid comprising a first base fluid and a first desensitizing agent into at least a portion of the subterranean formation, wherein the first desensitizing agent is present in the first base fluid at a first concentration; and then introducing a treatment fluid comprising a second base fluid and a second desensitizing agent

into at least a portion of the subterranean formation, wherein the second desensitizing agent is present in the second base fluid at a second concentration, and wherein the first concentration is higher than the second concentration.

[0103] In some embodiments, a method of desensitizing a subterranean formation may generally include the steps of: providing a wellbore penetrating a subterranean formation; introducing a leading-edge fluid comprising a first base fluid and a first desensitizing agent into a first portion of the subterranean formation, wherein the first desensitizing agent is present in the first base fluid at a first concentration; then introducing a treatment fluid comprising a second base fluid and a second desensitizing agent into the first portion of the subterranean formation, wherein the second desensitizing agent is present in the second base fluid at a second concentration, and wherein the first concentration is higher than the second concentration; then diverting fluid flow from the first portion of the subterranean formation to a second portion of the subterranean formation; then introducing a second leading-edge fluid comprising a third base fluid and a third desensitizing agent into the second portion of the subterranean formation, wherein the third desensitizing agent is present in the third base fluid at a third concentration; and then second introducing a treatment fluid comprising a fourth base fluid and a fourth desensitizing agent into the second portion of the subterranean formation, wherein the fourth desensitizing agent is present in the fourth base fluid at a second concentration, and wherein the third concentration is higher than the fourth concentration.

[0104] It should be noted that while this disclosure is drawn to desensitizing problematic formations, one skilled in the art with the benefit of this disclosure could adapt the methods provided herein for other multi-stage treatments of subterranean formations. Further many of the advantages disclosed herein may translate to the adapted methods including, but not limited to, effective penetration of a treatment deeper into the subterranean formation while decreasing the overall concentration of treatment fluid components. This reduction in the amount of treatment fluid components used can result in a significant cost savings for the operator and may help reduce the environmental impact of the treatment.

[0105] To facilitate a better understanding of the present invention, the following examples of preferred embodiments are given. In no way should the following examples be read to limit, or to define, the scope of the invention.

EXAMPLES

Example 1

[0106] X-Ray analysis of the field shale samples in South Texas revealed a clay concentration of about 40% to 50% with about 1% of the clay content identified as swelling clay. Based on this information, the following treatment recommendations were made:

[0107] (a) Use 1% v/v of CLA-WEB™ clay-stabilization additive in the first 5% of the fracturing treatment volume as the spearhead fluid. Thus, for a 500,000-gal fracturing treatment volume, an amount of 250 gal of CLA-WEB™ clay-stabilization additive was used in mixing with 25,000 gal of fresh water to prepare the 1% v/v CLA-WEB™ clay-stabilization additive solution.

[0108] (b) Use 0.05% v/v of CLA-WEB™ clay-stabilization additive in the remainder of the fracturing treatment

volume, or mix 250 gal of CLA-WEB™ clay-stabilization additive with the remaining 475,000 gal of fluid.

Example 2

[0109] For a well located in Saudi, X-ray diffraction analysis (Table 1) indicates only trace amounts of smectite clay in the obtained shale samples with a significant amount of mixed layers which may contain swelling clays.

TABLE 1

	Interval Depth	
	13,419.3'	13,582.5'
Quartz	37%	46%
K-feldspar	3%	3%
Na-feldspar	3%	4%
Dolomite	27%	2%
Pyrite	6%	6%
Kaolinite	3%	3%
Chlorite	trace	trace
Muscovite	trace	1%
Illite	12%	22%
Mixed layer	7%	7%
Smectite	trace	trace

[0110] Shale samples of the two intervals were crushed and sieved to obtained mesh size less than 200 U.S. mesh. Equal amounts of each sample was mixed to form a homogeneous blend which was used to form a sand pack column with the composition of 85% (w/w) of 70/170-mesh quartz sand, 10% (w/w) of silica flour, and 5% (w/w) of crushed, mixed shale samples. Flow tests were performed through the packed columns to evaluate the desensitize performance of 1% (v/v) and 3% (v/v) CLA-WEB™ clay-stabilization additive solutions. The series of treatment fluids and volumes are listed in Table 2. All fluids were injected through the column at 10 mL/min flow rate.

TABLE 2

Injected Fluids	Injected Volume (mL)
3% KCl brine	100
3% CLA-WEB™ clay-stabilization additive	200
3% KCl brine	50
Fresh water	60
3% KCl brine	100

[0111] A decrease in permeability of brine after exposure to fresh water comparing with brine pressure after treatment of 1% CLA-WEB™ clay-stabilization additive solution indicates that this 1% CLA-WEB™ clay-stabilization additive concentration was not sufficient for clay protection, which will result in permeability reduction. The treatment with 3% CLA-WEB™ clay-stabilization additive solution indicates this CLA-WEB™ clay-stabilization additive concentration was more appropriate to minimize any potential of permeability damage.

[0112] Based on the results of these tests, it was recommended that a concentration of 5% (v/v) of CLA-WEB™ clay-stabilization additive be used in the pad fluid of the fracturing treatment, and a concentration of 0.2% (v/v) of CLA-WEB™ clay-stabilization additive be used in the remainder of the fracturing fluid carrying proppant.

[0113] Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered, combined, or modified and all such variations are considered within the scope and spirit of the present invention. While compositions and methods are described in terms of "comprising," "containing," or "including" various components or steps, the compositions and methods can also "consist essentially of" or "consist of" the various components and steps. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, "from about a to about b," or, equivalently, "from approximately a to b," or, equivalently, "from approximately a-b") disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles "a" or "an," as used in the claims, are defined herein to mean one or more than one of the element that it introduces. If there is any conflict in the usages of a word or term in this specification and one or more patent or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

The invention claimed is:

1. A method of desensitizing a subterranean formation, the method comprising:

providing a wellbore penetrating a subterranean formation; introducing a leading-edge fluid comprising a first base fluid and a first desensitizing agent into at least a portion of the subterranean formation, wherein the first desensitizing agent is present in the first base fluid at a first concentration; and

then introducing a treatment fluid comprising a second base fluid and a second desensitizing agent into at least a portion of the subterranean formation, wherein the second desensitizing agent is present in the second base fluid at a second concentration, and wherein the first concentration is higher than the second concentration.

2. The method of claim 1, wherein the first concentration ranges from about 0.01% to about 60% v/v of the first desensitizing agent to the first base fluid.

3. The method of claim 1, wherein the first concentration changes over time in a manner selected from the group consisting of a gradient change, a step-wise change, and any combination thereof.

4. The method of claim 1, wherein the first concentration is about 2 to about 5000 times greater than the second concentration.

5. The method of claim 1, wherein the second concentration ranges from about 0.0001% to about 20% v/v of the second desensitizing agent to the second base fluid.

6. The method of claim 1, wherein the second concentration changes over time in a manner selected from the group consisting of a gradient change, a step-wise change, and any combination thereof.

7. The method of claim 1 further comprising:

introducing a transition fluid comprising a third base fluid and a third desensitizing solution that comprises a third desensitizing agent between the introduction of the leading-edge fluid and the treatment fluid, wherein the third desensitizing agent is present in the third base fluid at a third concentration.

8. The method of claim 7, wherein the third concentration changes over time in a manner selected from the group consisting of a gradient change, a step-wise change, and any combination thereof.

9. The method of claim 1, wherein the first desensitizing agent comprises at least one selected from the group consisting of: an inorganic acid, a salt, a polyelectrolyte, a multivalent ion, an inorganic base, a strong base, an oxide, a resin, a surfactant, a cationic polymer, a methyl glucoside, a polyglycerol, a polyglycol, an emulsion facilitating particle, a chelating agent, a phosphine, a soluble organic stabilizing compound, a silica control agent, an embrittlement modification agent, a surface modification agent, a microparticle, a nanoparticle, and any combination thereof.

10. The method of claim 1, wherein the second desensitizing agent comprises at least one selected from the group consisting of: an inorganic acid, a salt, a polyelectrolyte, a multivalent ion, an inorganic base, a strong base, an oxide, a resin, a surfactant, a cationic polymer, a methyl glucoside, a polyglycerol, a polyglycol, an emulsion facilitating particle, a chelating agent, a phosphine, a soluble organic stabilizing compound, a silica control agent, an embrittlement modification agent, a surface modification agent, a microparticle, a nanoparticle, and any combination thereof.

11. The method of claim 1, wherein the first desensitizing agent and the second desensitizing agent are different compositions.

12. The method of claim 1, wherein the leading-edge fluid and treatment fluid contain a same desensitizing agent such that the same desensitizing agent is from about 0.01% to about 60% v/v in the leading-edge fluid and the same desensitizing agent is from about 0.0001% to about 20% v/v in the treatment fluid.

13. The method of claim 1, wherein introducing the leading-edge fluid is performed at a fracture pressure.

14. The method of claim 1, wherein the leading-edge fluid further comprises a proppant.

15. The method of claim 1, wherein introducing the treatment fluid is performed at a fracture pressure.

16. The method of claim 1, wherein the treatment fluid further comprises a proppant.

17. A method of remedially desensitizing a subterranean formation, the method comprising:

providing a wellbore penetrating a subterranean formation that comprises a plurality of formation faces, the formation faces having undergone deleterious chemical and/or physical changes;

introducing a leading-edge fluid comprising a first base fluid and a first desensitizing agent into at least a portion of the subterranean formation, wherein the first desensitizing agent is present in the first base fluid at a first concentration; and

then introducing a treatment fluid comprising a second base fluid and a second desensitizing agent into at least a portion of the subterranean formation, wherein the second desensitizing agent is present in the second base fluid at a second concentration, and wherein the first concentration is higher than the second concentration.

18. A method of desensitizing a subterranean formation, the method comprising:

providing a wellbore penetrating a subterranean formation;
introducing a leading-edge fluid comprising a first base fluid and a first desensitizing agent into a first portion of the subterranean formation, wherein the first desensitizing agent is present in the first base fluid at a first concentration;

then introducing a treatment fluid comprising a second base fluid and a second desensitizing agent into the first portion of the subterranean formation, wherein the second desensitizing agent is present in the second base fluid at a second concentration, and wherein the first concentration is higher than the second concentration;

then diverting fluid flow from the first portion of the subterranean formation to a second portion of the subterranean formation;

then introducing a second leading-edge fluid comprising a third base fluid and a third desensitizing agent into the second portion of the subterranean formation, wherein the third desensitizing agent is present in the third base fluid at a third concentration; and

then second introducing a treatment fluid comprising a fourth base fluid and a fourth desensitizing agent into the second portion of the subterranean formation, wherein the fourth desensitizing agent is present in the fourth base fluid at a second concentration, and wherein the third concentration is higher than the fourth concentration.

19. The method of claim **18**, wherein diverting the fluid flow involves at least one selected from the group consisting of: a plugging agent, a plug, a packer, a bridge plug, a frac plug, plugging agent, a perf ball, a gel, a plugging foam, a diverting agent, a degradable diverting agent, and any combination thereof.

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