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(73) Patenthaver: **Flex-chem Holding Company LLC, 700 N. Wilson Rd., Weatherford, OK 73096, USA**

(72) Opfinder: **CONWAY, Andrew, Bryce, 1501 timbercreek Drive, Weatherford, OK 73096, USA**

(74) Fuldmægtig i Danmark: **CHAS. HUDE A/S, Langebrogade 3B, 1411 København K, Danmark**

(54) Benævnelse: **SLICKVANDFRAKTURERING VED ANVENDELSE AF TIDSFORSINKET FRIGIVELSE AF METALKOMPLEKSDANNENDE MIDDEL**

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DESCRIPTION

[0001] This application is being filed as a PCT International application on 04 September 2015, and claims the benefit of U.S. Provisional Application No. 62/045,967, filed September 4, 2014.

INTRODUCTION

[0002] Water-based fracturing fluids containing a friction-reducing polymer are called "slick water." Slick-water fracturing of oil and gas wells is conducted by pumping at high pressures and high velocities through a vertical and, usually, a horizontal section of a well. The well contains a well casing and, in some wells, tubing inside the casing. Perforations or ports in the casing are adjacent to targeted intervals of subterranean formations containing a hydrocarbon. Hydraulic pressure exerted on the formation, above the fracturing gradient, causes the formation to fracture, creating an extensive fracture network. Most often these formations have minimal permeability and include sandstone, shale or coals. Once the fracture or crack is initiated, pumping is continued, allowing the fracture to propagate.

[0003] Once the fracture has gained sufficient fracture width, a proppant such as sand is added to the fluid and is transported to the fracture system, partially filling the fracture network. After the desired amount of proppant is placed in the fracture, additional water-based fluid is pumped to flush the casing of any proppant that may have settled in the casing. On completion of the fracturing process, the well is opened, allowing a portion of the fluid to be recovered. As the pressure is relieved, the fracture closes onto the proppant, creating a conductive pathway needed to accelerate oil and gas recovery from the formation.

[0004] The water-based fracturing fluid can contain polymer and multiple chemical additives. The additives may include biocide, scale inhibitor, clay control additive, oxygen scavenger and surfactant that assist fluid recovery. To keep the fracturing treatments affordable, only minimal amounts of these additives are used. Each additive is normally liquid-based and is metered separately into the treatment fluid and mixed with water and other additives in the blender. The blender includes a 5- to 15-barrel tub with agitation devices. The additive concentrations are commonly expressed as gallons of additive per 1000 gallons of water (abbreviated as gallons per thousand or gpt). The additives typically are composed of a chemical that provides the desired function such as scale inhibition and a solvent, commonly water, alcohol or oil.

[0005] The polymer in slick-water fluids provides friction reduction during pumping of the fluid into a well. Friction reducers are commonly delivered to a well site as invert polymer emulsions (oil external) dispersions of polyacrylamide copolymers, such as 30% anionic polyacrylamide, non-ionic polyacrylamide, or cationic polyacrylamide. Typical loadings range from 0.1 to 1.0 gpt and the polymer activity typically ranges from 20% to 40% (by weight). Addition of friction reducers to the water allows the fluid to be pumped at higher velocities with the same surface pressure by maintaining laminar flow at the higher flow rates, minimizing pressure losses.

[0006] US 2009/298721 discloses a method that comprises: introducing a treatment fluid into a subterranean formation, wherein the treatment fluid comprises water and a concentrated polymer composition comprising a complexing agent and a friction reducing polymer. Also disclosed is a method that comprises combining at least water and a concentrated polymer composition to form a treatment fluid, wherein the concentrated polymer composition comprises a complexing agent and a friction reducing polymer: and introducing the treatment fluid into a subterranean formation. Also disclosed is a concentrated polymer composition comprising: a friction reducing polymer in an amount of about 15% to about 60% by weight of the composition; and a complexing agent.

[0007] US6527051 discloses encapsulated water soluble chemicals for use in controlled time release applications, methods of encapsulating the chemicals and methods of using the encapsulated chemicals are provided. The methods of encapsulating the chemicals are basically comprised of forming a first coating of a dry hydrophobic film forming material or a sparingly soluble material which provides a dry shield on the chemical and then forming a second coating of a porous cross-linked hydrophilic polymer on the first coating which prevents the substantial dissolution of the resulting encapsulated chemical for a selected period of time.

SLICK-WATER FRACTURING USING TIME RELEASE METAL-COMPLEXING AGENT

[0008] This disclosure describes embodiments of methods and time-release compositions that can be used to prevent the interaction between the friction-reducing polymer and naturally occurring or introduced metal ions, thereby improving the performance of a slick-water fracturing operation. In one aspect, this disclosure describes a slick-water fracturing fluid comprising a friction reducer and a time-released form of a metal complexing agent.

[0009] In another aspect this disclosure describes a method for slick-water fracturing, including adding a time-released form of a metal-complexing agent to a slick-water fracturing fluid. In the method, the time-release form of the metal-complexing agent is added in an amount of about 453.5 grams per 3.785 kiloliters to 22679.6 grams per 3.785 kiloliters (1 pound per thousand gallons to about 50 pounds per thousand gallons). The method also includes introducing the combined slick-water fracturing fluid and time-released form of a metal complexing agent into a subterranean zone.

[0010] In yet another aspect, this disclosure describes a slick-water fracturing fluid including a friction reducing polymer and a time-released form of a metal complexing agent, where the time released form of the metal complexing agent is present in the slick-water fracturing fluid at about 45.35 grams per 3.785 kiloliters to 22679.6 grams per 3.785 kiloliters (0.1 pound per thousand gallons to about 50 pounds per thousand gallons).

[0011] These and various other features as well as advantages which characterize the systems and methods described herein will be apparent from a reading of the following

detailed description and a review of the associated drawings. Additional features are set forth in the description which follows, and in part will be apparent from the description, or may be learned by practice of the technology. The benefits and features of the technology will be realized and attained by the structure particularly pointed out in the written description and claims hereof as well as the appended drawings.

[0012] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory and are intended to provide further explanation of the invention as claimed.

DETAILED DESCRIPTION

[0013] Before the slick water fracturing systems are disclosed and described, it is to be understood that this disclosure is not limited to the particular structures, process steps, or materials disclosed herein, but is extended to equivalents thereof as would be recognized by those ordinarily skilled in the relevant arts. It should also be understood that terminology employed herein is used for the purpose of describing particular embodiments only and is not intended to be limiting. It must be noted that, as used in this specification, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a lithium hydroxide" is not to be taken as quantitatively or source limiting, reference to "a step" may include multiple steps, reference to "producing" or "products" of a reaction should not be taken to be all of the products of a reaction, and reference to "reacting" may include reference to one or more of such reaction steps. As such, the step of reacting can include multiple or repeated reaction of similar materials to produce identified reaction products

[0014] This disclosure describes embodiments of methods and time-release compositions that can be used to prevent the interaction between the friction-reducing polymer and naturally occurring or introduced metal ions, thereby improving the performance of a slick-water fracturing operation.

[0015] In slick-water fracturing of hydrocarbon-bearing shales, the inventor has observed that the metal-rich environment of the gas shales reduces the effectiveness of slick-water fracturing. Without being held to a particular theory, it appears that the metals of the shale are interacting with the polymer in some way as to negatively impact the fracturing operation, possibly by forming a metal-polymer complex that reduces the polymer's effectiveness as a friction reducer, chemically or physically interact with the friction reducer in ways that produce undesirable effects or making it more difficult to remove the friction reducer from the fracture and wellbore after completion of the fracturing operation.

[0016] As mentioned above, this disclosure describes embodiments of methods and compositions that can be used to prevent the interaction between the polymer and naturally occurring metal ions, thereby improving the performance of a slick-water fracturing operation.

In one embodiment, a metal-complexing agent, such as citric acid, may be provided as an additional additive to the slick-water fracturing operation. It is anticipated that the metal-complexing agent will preferentially bind with the metals found in the clay, thereby freeing the polymer to continue to perform its function as a frictionreducer.

[0017] The metal-complexing agent is provided in a form, type or delivery system that prevents loss of the agent prior to delivery at the shale (i.e., during the injection process). In this embodiment, the metal-complexing agent is encapsulated with a coating, such as a dry hydrophobic film forming material or a dry sparingly soluble material and particulate silica, may be formed on the particulate solid complexing agent. For example, solid citric acid may be encapsulated in a paraffin or cottonseed oil coating. Alternatively, the release time could be controlled or influenced by differential solubility or rate of dissolution of the metal-complexing agent in the transporting fluid as a result of injecting it into the wellbore and/or reservoir. For example, EDTA is slowly soluble at room temperature or low temperatures in which it could be mixed, and the solubility increases as the temperature of the fluid increases in the wellbore or reservoir.

[0018] A second coating is also used comprising a porous cross-linked hydrophilic polymer such that when contacted with water it prevents the substantial dissolution of the encapsulated chemical for a selected time period. In another embodiment the metal-complexing agent could be preserved by a coating that can be disrupted by pressure changes or mechanical forces such as fracture closure. Several time-release encapsulation materials and techniques for use in hydraulic fracturing are known in the art and any suitable technique may be used that delivers the metal-complexing agent to the shale such that it is released at approximately the time that the polymer is being exposed to the metal-bearing formation. In another such an embodiment loss of the metal-complexing agent could be prevented prior to delivery at the shale by coating or adsorbing the metal-complexing agent to materials that release in response to changes in environmental redox potential, pH or ion exchange.

[0019] In a specific embodiment of this technology, solid citric acid may be provided in a time release form and added to the slick-water fracturing fluid in an amount of 45.35 grams per 3.785 kiloliters to 22679.6 grams per 3.785 kiloliters (0.1-50 pounds per thousand gallons (1b./Mgal)). More particularly, between 226.796 grams per 3.785 kiloliters and 11339.8 grams per 3.785 kiloliters (0.5 and 25 lb./Mgal) of slick-water fracturing fluid may be used in the first half of each treatment stage to place. And, in an embodiment about 907.185 grams per 3.785 kiloliters to 2267.96 grams per 3.785 kiloliters (2-5 1b./Mgal] of slick-water fracturing fluid may be used in the first half of each treatment stage to place more of the treatment allocation at maximum depth in the propped fracture, and then between 226.796 grams per 3.785 kiloliters and 453.592 grams per 3.785 kiloliters (0.5-1 1b./Mgal) of slick-water fracturing fluid may be used during the remainder of the stage. It is anticipated that the time release of the citric acid will preferentially form complexes with any available metal ions from the formation and, thereby, improve the fracturing achieved by the operation.

[0020] In some embodiments, the metal-complexing agent is a chelating agent, an alkali metal

salt thereof, a non-alkali metal salt thereof, or any combination thereof may be included in the treatment fluids described herein. In some embodiments, the chelating agent may be biodegradable. Although use of a biodegradable chelating agent may be particularly advantageous in some embodiments of the present disclosure, there is no requirement to do so, and, in general, any suitable chelating agent may be used. As used herein, the term "biodegradable" refers to a substance that can be broken down by exposure to environmental conditions including native or non-native microbes, sunlight, air, heat, and the like. Use of the term "biodegradable" does not imply a particular degree of biodegradability, mechanism of biodegradability, or a specified biodegradation half-life.

[0021] In some embodiments, suitable chelating agents may include common chelating agent compounds such as, for example, ethylenediaminetetraacetic acid (EDTA), propylenediaminetetraacetic acid (PDTA), nitrilotriacetic acid (NTA), N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethyliminodiacetic acid (HEIDA), cyclohexylenediaminetetraacetic acid (CDTA), diphenylaminesulfonic acid (DPAS), ethylenediaminedi(o-hydroxyphenylacetic) acid (EDDHA), glucoheptonic acid, gluconic acid, citric acid, any salt thereof, any derivative thereof, and the like. It is to be noted that NTA may be considered to be a biodegradable compound, but it may have undesirable toxicity issues.

[0022] In some embodiments, suitable chelating agents may include biodegradable chelating agents such as, for example, glutamic acid diacetic acid (GLDA), methylglycine diacetic acid (MGDA), β-alanine diacetic acid (β-ADA), ethylenediaminedisuccinic acid, S,S-ethylenediaminedisuccinic acid (EDDS), iminodisuccinic acid (IDS), hydroxyiminodisuccinic acid (HIDS), polyamino disuccinic acids, N-bis[2-(1,2- dicarboxyethoxy)ethyl]glycine (BCA6), N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid (BCA5), N-bis[2-(1,2-dicarboxyethoxy)ethyl]methylglycine (MCBA5), N-tris[(1,2-dicarboxyethoxy)ethyl]amine (TCA6), N-methyliminodiacetic acid (MIDA), iminodiacetic acid (IDA), N-(2-acetamido)iminodiacetic acid (ADA), hydroxymethyl-iminodiacetic acid, 2-(2-carboxyethylamino) succinic acid (CEAA), 2-(2-carboxymethylamino) succinic acid (CMAA), diethylenetriamine- N,N''-disuccinic acid, triethylenetetramine-N,N‴-disuccinic acid, 1,6- hexamethylenediamine-N,N'-disuccinic acid, tetraethylenepentamine-N,N⁗- disuccinic acid, 2-hydroxypropylene-1,3-diamine-N,N'-disuccinic acid, 1,2- propylenediamine-N,N'-disuccinic acid, 1,3-propylenediamine-N,N'-disuccinic acid, cis-cyclohexanediamine-N,N'-disuccinic acid, trans-cyclohexanediamine- N,N'-disuccinic acid, ethylenebis(oxyethylenenitrilo)-N,N'-disuccinic acid, glucoheptanoic acid, cysteic acid-N,N-diacetic acid, cysteic acid-N-monoacetic acid, alanine-N-monoacetic acid, N-(3-hydroxysuccinyl) aspartic acid, N-[2-(3-hydroxysuccinyl)]-L-serine, aspartic acid-N,N-diacetic acid, aspartic acid-N-monoacetic acid, any salt thereof, any derivative thereof, or any combination thereof.

[0023] In an alternative embodiment, the metal-complexing agent may be a suitable sequestering agent such as polysuccinimide, polyaspartic acid, and polymers, oligomers, chains or block-copolymers of the twenty two essential amino acids containing metal complexing groups such as carboxylic acids, phosphonic acids, sulfonic acids and boronic

acids.

[0024] Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention.

[0025] As used herein, "about" refers to a degree of deviation based on experimental error typical for the particular property identified. The latitude provided the term "about" will depend on the specific context and particular property and can be readily discerned by those skilled in the art. The term "about" is not intended to either expand or limit the degree of equivalents which may otherwise be afforded a particular value. Further, unless otherwise stated, the term "about" shall expressly include "exactly," consistent with the discussions regarding ranges and numerical data. Concentrations, amounts, and other numerical data may be expressed or presented herein in a range format..

[0026] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0027] It will be clear that the systems and methods described herein are well adapted to attain the ends and advantages mentioned as well as those inherent therein. Those skilled in the art will recognize that the methods and systems within this specification may be implemented in many manners and as such is not to be limited by the foregoing exemplified embodiments and examples. In other words, functional elements being performed by a single or multiple components, in various combinations of hardware and software, and individual functions can be distributed among software applications at either the client or server level. In this regard, any number of the features of the different embodiments described herein may be combined into one single embodiment and alternate embodiments having fewer than or more than all of the features herein described are possible.

[0028] While various embodiments have been described for purposes of this disclosure, various changes and modifications may be made which are well within the scope of the present invention. Numerous other changes may be made which will readily suggest themselves to those skilled in the art.

REFERENCES CITED IN THE DESCRIPTION

Cited references

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

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Patentkrav

1. Slickvandfraktureringsfluid der omfatter:

et friktionsreducerende middel; og

en tidsforsinket form af et metalkompleksdannende middel, hvilket metalkompleksdannende middel er indkapslet af en første coating og en anden coating, hvor den anden coating er en porøs tværbundet hydrofil polymer.

2. Slickvandfraktureringsfluidet ifølge krav 1, hvori det metalkompleksdannende middel er citronsyre.

3. Slickvandfraktureringsfluidet ifølge krav 2, hvor den første coating er en paraffincoating.

4. Slickvandfraktureringsfluidet ifølge krav 2, hvor den første coating er en coating af bomuldsfrøolie.

5. Slickvandfraktureringsfluid ifølge et hvilket som helst af de foregående krav, hvor det metalkompleksdannende middel er til stede i slickvandfraktureringsfluidet i en mængde på 45,35 gram pr. 3,785 kiloliter (0,1 pund pr. tusinde gallons) til 22679,6 gram pr. (50 pund pr. tusinde gallons).

6. Slickvandfraktureringsfluidet ifølge krav 5, hvori det metalkompleksdannende middel er til stede i slickvandfraktureringsfluidet i en mængde på 226,796 gram pr. 3,785 kiloliter (0,5 pund pr. tusinde gallons) til 11339,8 gram pr. 3,785 kiloliter (25 pund pr. tusinde gallons).

7. Slickvandfraktureringsfluidet ifølge krav 5, hvor det metalkompleksdannende middel er til stede i slickvandfraktureringsfluidet i en mængde på 907,185 gram pr. 3,785 kiloliter (2 pund pr. tusinde gallons) til 2267,96 gram pr. 3.785 kiloliter (5 pund pr. tusinde gallons).

8. Slickvandfraktureringsfluidet ifølge krav 1, hvor

det friktionsreducerende middel er en friktionsreducerende polymer; og den tidsforsinkede form af det metalkompleksdannende middel er til stede i slickvandfraktureringsfluidet med 45,35 gram pr. 3,785 kiloliter (0,1 pund pr. tusinde gallons) til 22679,6 gram pr. 3,785 kiloliter (50 pund pr. tusinde gallons).

9. Slickvandfraktureringsfluid ifølge krav 2 og 8, hvor det tidsforsinkede metalkompleksdannende middel er fast citronsyre.

10. Slickvandfraktureringsfluidet ifølge krav 9, hvor den første coating er et tørt hydrofobt filmdannende materiale.

11. Slickvandfraktureringsfluidet ifølge krav 10, hvor den tidsforsinkede form af det metalkompleksdannende middel er til stede i slickvandfraktureringsfluidet med 907,185 gram pr. 3,785 kiloliter (2 pund pr. tusinde gallons) til 2267,96 gram pr. 3,785 kiloliter (5 pund pr. tusinde gallons).

12. Slickvandfraktureringsfluidet ifølge krav 1, hvor det metalkompleksdannende middel er til stede i slickvandfraktureringsfluidet i en mængde på 45,35 gram pr. 3,785 kiloliter (0,1 pund pr. tusinde gallons) til 22679,6 gram pr. 3,785 kiloliter (50 pund pr. tusinde gallons), og hvor det tidsforsinkede metalkompleksdannende middel er valgt fra gruppen, der består af: ethylendiamintetraeddikesyre (EDTA), propylendiamintetraeddikesyre (PDTA), nitrilotrieddikesyre (NTA), N-(2-hydroxyethyl)ethylendiamintrieddikesyre (HEDTA) , diethylentriaminpentaeddikesyre (DPTA), hydroxyethyliminodieddikesyre (HEIDA), cyclohexylendiamintetraeddikesyre (CDTA), diphenylaminsulfonsyre (DPAS), ethylendiamindi(o-hydroxyphenyleddikesyre) (EDDHA), glucoheptonsyre, gluconsyre, citronsyre og salte deraf.

13. Slickvandfraktureringsfluidet ifølge krav 1, hvori det metalkompleksdannende middel er til stede i slickvandfraktureringsfluidet i en mængde på 45,35 gram pr. 3,785 kiloliter (0,1 pund pr. tusinde gallons) til 22679,6 gram pr. pr. 3,785 kiloliter (50 pund pr. tusind gallons), og hvori det tidsforsinkede metalkompleksdannende middel er valgt fra gruppen, der består af: glutaminsyredieddikesyre (GLDA), methylglycindieddikesyre (MGDA), β-alanindieddikesyre (β-ADA), ethylendiamindisuccinsyre, S,S-ethylendiamindisuccinsyre (EDDS), iminodisuccinsyre (IDS), hydroxyiminodisuccinsyre (HIDS), polyaminodisuccinsyre, N-bis[2-(1,2-dicarboxyethoxy)ethyl]glycin (BCA6), N-bis[2 -(1,2-dicarboxyethoxy)ethyl]asparaginsyre (BCA5), N-bis[2-(1,2-dicarboxyethoxy)ethyl]methylglycin (MCBA5), N-tris[(1,2-dicarboxyethoxy)ethyl]amin (TCA6), N-methyliminodieddikesyre (MIDA), iminodieddikesyre (IDA),N-(2-acetamido)iminodieddikesyre (ADA), hydroxymethyliminodieddikesyre, 2-(2-carboxyethylamino)succinsyre (CEAA), 2-(2-carboxymethylamino)succinsyre (CMAA), diethylentriamin-N,N''-disuccinsyre, triethylentetramin-N,N‴-disuccinsyre, 1,6-hexamethylendiamin-N,N'-disuccinsyre, tetraethylenpentamin-N, N''''-disuccinsyre, 2-hydroxypropylen-1,3-diamin-N,N'-disuccinsyre, 1,2-propylendiamin-N,N'-disuccinsyre, 1,3-propylendiamin-N,N'- disuccinsyre, cis-cyclohexandiamin-N,N'-disuccinsyre, trans-cyclohexandiamin-N,N'-disuccinsyre, ethylenbis(oxyethylennitrilo)-N,N'-disuccinsyre, glucoheptansyre, cysteinsyre-N,N-dieddikesyre, cysteinsyre-N-monoeddikesyre, alanin-N-monoeddikesyre, N-(3-hydroxysuccinyl)asparaginsyre, N-[2-(3-hydroxysuccinyl)]-L-serin, asparaginsyre-N,N-dieddikesyre, asparaginsyre-N-monoeddikesyre og salte deraf.

14. Slickvandfraktureringsfluid ifølge krav 1, hvor den første coating er et tørt hydrofobt filmdannende materiale.

15. Fremgangsmåde til slickvandfrakturering der omfatter:

at tilsætte en tidsforsinket form af et metalkompleksdannende middel til et slickvandfraktureringsfluid, hvilket metalkompleksdannende middel er

indkapslet af en første coating og en anden coating, hvor den anden coating er en porøs tværbundet hydrofil polymer;

hvilken tidsforsinkede form af det metalkompleksdannende middel tilsættes i en mængde på 45,35 gram pr. 3,785 kiloliter (0,1 pund pr. tusinde gallons) til 22679,6 gram pr. 3,785 kiloliter (50 pund pr. tusinde gallons); og

at indføre det kombinerede slickvandfraktureringsfluid og den tidsforsinkede form af det metalkompleksdannende middel i en underjordisk zone.

16. Fremgangsmåden til slickvandfrakturering ifølge krav 15, hvor det metalkompleksdannende middel er citronsyre.

17. Fremgangsmåden til slickvandfrakturering ifølge krav 16, hvor den tidsforsinkede form af det metalkompleksdannende middel tilsættes i en mængde på 907,185 gram pr. 3,785 kiloliter (2 pund pr. tusinde gallons) til 2267,96 gram pr. pr. 3,785 kiloliter (5 pund pr. tusinde gallons).