



US 20140367099A1

(19) **United States**

(12) **Patent Application Publication**
George et al.

(10) **Pub. No.: US 2014/0367099 A1**

(43) **Pub. Date: Dec. 18, 2014**

(54) **DEGRADATION OF POLYLACTIDE IN A WELL TREATMENT**

(71) Applicant: **Halliburton Energy Services, Inc.**,
Houston, TX (US)

(72) Inventors: **Shoy Chittattukara George**, Thrissur
(IN); **Vijaya Kumar Patnana**,
Visakhapatnam (IN)

(21) Appl. No.: **13/919,071**

(22) Filed: **Jun. 17, 2013**

Publication Classification

(51) **Int. Cl.**
E21B 43/16 (2006.01)

(52) **U.S. Cl.**
CPC **E21B 43/16** (2013.01)
USPC **166/276; 166/300**

(57) **ABSTRACT**

Methods of treating a portion of a well include the steps of: (A) depositing a solid particulate into the portion of the well, wherein the solid particulate comprises an aliphatic polyester, preferably a polylactide; and (B) contacting the particulate deposited in the portion of the well with a treatment fluid comprising: (i) water; (ii) a source of a strong alkali; and (iii) a source of a strong oxidizer. The steps of depositing and contacting can be with a single treatment fluid or separate treatment fluids.

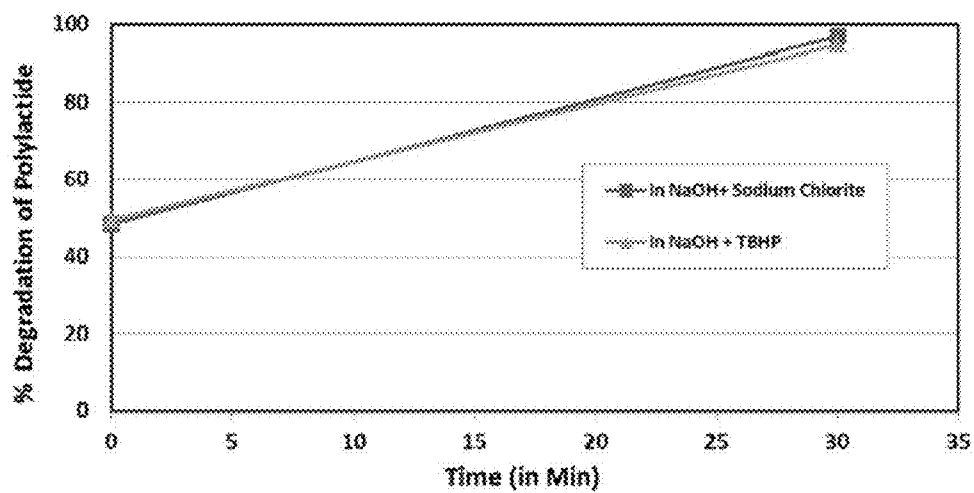


Figure 1

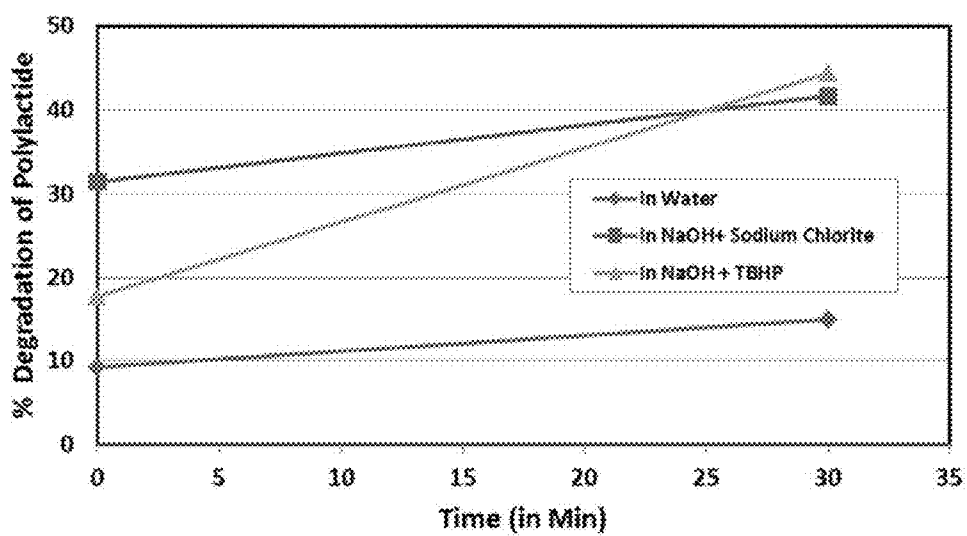


Figure 2

DEGRADATION OF POLYLACTIDE IN A WELL TREATMENT

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] Not applicable.

TECHNICAL FIELD

[0002] The inventions are in the field of producing crude oil or natural gas from subterranean formations. More specifically, the inventions generally relate to methods for leak-off control or diversion applications in a well.

BACKGROUND

[0003] Aliphatic polyesters, such as polylactides, can be used for several well treatment applications such as diversion, fluid loss control, and plugging of natural fractures or perforations while pumping a drilling fluid or treatment fluid or applications such as acidizing.

[0004] For example, aliphatic polyesters, are used as degradable particulates in drilling fluids or treatment fluids that form a filtercake to provide fluid loss control. For example, a polylactide particulate can be added to a drilling or treatment fluid in an amount necessary to give the desired fluid-loss control.

[0005] By way of another example, a polyester particulate can be used in a treatment fluid to help provide diversion during a variety of well-treatment operations, including, for example, matrix acidizing or acid fracturing formations to help achieve good zonal coverage of the treatment fluid. The solid particulate can be used for diverting fluid between high permeability contrast zones.

[0006] In addition, such particulate can be used for diverting a fluid in high permeability contrast zones.

[0007] After application of a filter cake or otherwise depositing a particulate in a treatment zone, however, it may be desirable to restore the permeability of the formation. For example, a filtercake should be degraded to restore permeability for producing from the zone. If the formation permeability of the desired producing zone is not restored, production levels from the formation can be significantly lower. Any filter cake or any solid or polymer filtration into the matrix of the zone resulting from a fluid-loss control treatment must be removed to restore the formation's permeability, preferably to its original level. This is often referred to as clean up.

[0008] The polyester particulate is degradable so that permeability of a potentially producing subterranean formation can be restored.

[0009] The time and ease of flow-back after depositing the solid particulate into a treatment zone depends on how quickly the degradation of treatment materials occurs.

[0010] At design temperatures lower than about 93° C. (200° F.), however, polyester particulates, such as polylactide particulates, are extremely slow to degrade, and the time frame might be unacceptable to the customer considering higher costs of rig time or shut-in time. For example, the degradation time to achieve about 70 to 80% degradation of polylactide is about 18 hours in non-acidic or acidic aqueous mediums at 93° C. (200° F.).

[0011] Although polylactide provides good performance in many applications, it would be highly desirable to reduce

shut-in time for the degradation before being able to put a well under flow back because of slow degradation of the polylactide.

[0012] Hence, there is a long-felt need for quick degradation solution for polyesters such as polylactide, especially at lower temperatures.

SUMMARY OF THE INVENTION

[0013] Methods of treating a portion of a well are provided, the methods including the steps of: (A) depositing a solid particulate into the portion of the well, wherein the solid particulate comprises an aliphatic polyester; and (B) contacting the particulate with a treatment fluid comprising: (i) water; (ii) a source of a strong alkali; and (iii) a source of a strong oxidizer. The steps of depositing and contacting can be with a single treatment fluid or separate treatment fluids.

[0014] In an embodiment of the invention, a method of treating a portion of a well includes the step of: introducing a treatment fluid into the portion of the well, wherein the treatment fluid comprises: (i) a solid particulate, wherein the solid particulate is deposited in the well, and wherein the solid particulate comprises an aliphatic polyester; (ii) water; (iii) a source of a strong alkali; and (iv) a source of a strong oxidizer.

[0015] In another embodiment, a method of treating a portion of a well includes the steps of: (A) introducing a first treatment fluid into the portion of the well, wherein the first treatment fluid comprises a solid particulate, wherein the solid particulate is deposited in the well, and wherein the solid particulate comprises an aliphatic polyester; and (B) before or after the step of introducing the first treatment fluid into the portion of the well, introducing a second treatment fluid into the portion of the well, whereby the second treatment fluid contacts the solid particulate in the portion of the well, and wherein the second treatment fluid comprises: (i) water; (ii) a source of a strong alkali; and (iii) a source of a strong oxidizer.

[0016] These and other aspects of the invention will be apparent to one skilled in the art upon reading the following detailed description. While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof will be described in detail and shown by way of example. It should be understood, however, that it is not intended to limit the invention to the particular forms disclosed, but, on the contrary, the invention is to cover all modifications and alternatives falling within the spirit and scope of the invention as expressed in the appended claims.

BRIEF DESCRIPTION OF THE DRAWING

[0017] The accompanying drawing is incorporated into the specification to help illustrate examples according to a presently preferred embodiment of the invention.

[0018] FIG. 1 is a graph showing the degradation percentage (x-axis) of polylactide in an alkali treatment fluid with sodium chlorite (square data points) or tert-butyl hydrogen peroxide ("TBHP") (triangular data points) at 200° F. as a function of time in minutes (y-axis).

[0019] FIG. 2 is a graph showing the degradation percentage (x-axis) of polylactide in alkali treatment fluid with sodium chlorite (square data points) or TBHP (triangular data points) at 80° F. as a function of time in minutes (y-axis).

DETAILED DESCRIPTION OF PRESENTLY
PREFERRED EMBODIMENTS AND BEST
MODE

Definitions and Usages

[0020] Interpretation

[0021] The words or terms used herein have their plain, ordinary meaning in the field of this disclosure, except to the extent explicitly and clearly defined in this disclosure or unless the specific context otherwise requires a different meaning.

[0022] If there is any conflict in the usages of a word or term in this disclosure and one or more patent(s) or other documents that may be incorporated by reference, the definitions that are consistent with this specification should be adopted.

[0023] The words “comprising,” “containing,” “including,” “having,” and all grammatical variations thereof are intended to have an open, non-limiting meaning. For example, a composition comprising a component does not exclude it from having additional components, an apparatus comprising a part does not exclude it from having additional parts, and a method having a step does not exclude it having additional steps. When such terms are used, the compositions, apparatuses, and methods that “consist essentially of” or “consist of” the specified components, parts, and steps are specifically included and disclosed. As used herein, the words “consisting essentially of,” and all grammatical variations thereof are intended to limit the scope of a claim to the specified materials or steps and those that do not materially affect the basic and novel characteristic(s) of the claimed invention.

[0024] The indefinite articles “a” or “an” mean one or more than one of the component, part, or step that the article introduces.

[0025] Whenever a numerical range of degree or measurement with a lower limit and an upper limit is disclosed, any number and any range falling within the range is also intended to be specifically disclosed. For example, every range of values (in the form “from a to b,” or “from about a to about b,” or “from about a to b,” “from approximately a to b,” and any similar expressions, where “a” and “b” represent numerical values of degree or measurement) is to be understood to set forth every number and range encompassed within the broader range of values.

[0026] It should be understood that algebraic variables and other scientific symbols used herein are selected arbitrarily or according to convention. Other algebraic variables can be used.

[0027] Terms such as “first,” “second,” “third,” etc. may be assigned arbitrarily and are merely intended to differentiate between two or more components, parts, or steps that are otherwise similar or corresponding in nature, structure, function, or action. For example, the words “first” and “second” serve no other purpose and are not part of the name or description of the following name or descriptive terms. The mere use of the term “first” does not require that there be any “second” similar or corresponding component, part, or step. Similarly, the mere use of the word “second” does not require that there be any “first” or “third” similar or corresponding component, part, or step. Further, it is to be understood that the mere use of the term “first” does not require that the element or step be the very first in any sequence, but merely that it is at least one of the elements or steps. Similarly, the mere use of the terms “first” and “second” does not necessarily require any sequence. Accordingly, the mere use of such terms does not

exclude intervening elements or steps between the “first” and “second” elements or steps, etc.

[0028] The control or controlling of a condition includes any one or more of maintaining, applying, or varying of the condition. For example, controlling the temperature of a substance can include heating, cooling, or thermally insulating the substance.

[0029] Oil or Gas Reservoirs

[0030] In the context of production from a well, “oil” and “gas” are understood to refer to crude oil and natural gas, respectively. Oil and gas are naturally occurring hydrocarbons in certain subterranean formations.

[0031] A “subterranean formation” is a body of rock that has sufficiently distinctive characteristics and is sufficiently continuous for geologists to describe, map, and name it.

[0032] A subterranean formation having a sufficient porosity and permeability to store and transmit fluids is sometimes referred to as a “reservoir.”

[0033] A subterranean formation containing oil or gas may be located under land or under the seabed off shore. Oil and gas reservoirs are typically located in the range of a few hundred feet (shallow reservoirs) to a few tens of thousands of feet (ultra-deep reservoirs) below the surface of the land or seabed.

[0034] Wells

[0035] A “well” includes a wellhead and at least one wellbore from the wellhead penetrating the earth. The “wellhead” is the surface termination of a wellbore, which surface may be on land or on a seabed.

[0036] A “well site” is the geographical location of a wellhead of a well. It may include related facilities, such as a tank battery, separators, compressor stations, heating or other equipment, and fluid pits. If offshore, a well site can include a platform.

[0037] The “wellbore” refers to the drilled hole, including any cased or uncased portions of the well or any other tubulars in the well. The “borehole” usually refers to the inside wellbore wall, that is, the rock surface or wall that bounds the drilled hole. A wellbore can have portions that are vertical, horizontal, or anything in between, and it can have portions that are straight, curved, or branched. As used herein, “uphole,” “downhole,” and similar terms are relative to the direction of the wellhead, regardless of whether a wellbore portion is vertical or horizontal.

[0038] A wellbore can be used as a production or injection wellbore. A production wellbore is used to produce hydrocarbons from the reservoir. An injection wellbore is used to inject a fluid, for example, liquid water or steam, to drive oil or gas to a production wellbore.

[0039] As used herein, introducing “into a well” means introducing at least into and through the wellhead. According to various techniques known in the art, tubulars, equipment, tools, or fluids can be directed from the wellhead into any desired portion of the wellbore.

[0040] As used herein, a “fluid” broadly refers to any fluid adapted to be introduced into a well for any purpose. A fluid can be, for example, a drilling fluid, a setting composition, a treatment fluid, or a spacer fluid. If a fluid is to be used in a relatively small volume, for example less than about 100 barrels (about 4,200 US gallons or about 16 m³), it is sometimes referred to as a wash, dump, slug, or pill.

[0041] Drilling fluids, also known as drilling muds or simply “muds,” are typically classified according to their base fluid, that is, the nature of the continuous phase. A water-

based mud ("WBM") has a water phase as the continuous phase. The water can be brine. A brine-based drilling fluid is a water-based mud in which the aqueous component is brine. In some cases, oil may be emulsified in a water-based drilling mud. An oil-based mud ("OBM") has an oil phase as the continuous phase. In some cases, a water phase is emulsified in the oil-based mud.

[0042] As used herein, the word "treatment" refers to any treatment for changing a condition of a portion of a wellbore or a subterranean formation adjacent a wellbore; however, the word "treatment" does not necessarily imply any particular treatment purpose. A treatment usually involves introducing a fluid for the treatment, in which case it may be referred to as a treatment fluid, into a well. As used herein, a "treatment fluid" is a fluid used in a treatment. The word "treatment" in the term "treatment fluid" does not necessarily imply any particular treatment or action by the fluid.

[0043] In the context of a well or wellbore, a "portion" or "interval" refers to any downhole portion or interval along the length of a wellbore.

[0044] A "zone" refers to an interval of rock along a wellbore that is differentiated from uphole and downhole zones based on hydrocarbon content or other features, such as permeability, composition, perforations or other fluid communication with the wellbore, faults, or fractures. A zone of a wellbore that penetrates a hydrocarbon-bearing zone that is capable of producing hydrocarbon is referred to as a "production zone." A "treatment zone" refers to an interval of rock along a wellbore into which a fluid is directed to flow from the wellbore. As used herein, "into a treatment zone" means into and through the wellhead and, additionally, through the wellbore and into the treatment zone.

[0045] As used herein, a "downhole" fluid (or gel) is an in-situ fluid in a well, which may be the same as a fluid at the time it is introduced, or a fluid mixed with another fluid downhole, or a fluid in which chemical reactions are occurring or have occurred in-situ downhole.

[0046] Fluid loss refers to the undesirable leakage of a fluid phase of any type of fluid into the permeable matrix of a zone, which zone may or may not be a treatment zone or production zone. Fluid-loss control refers to treatments designed to reduce such undesirable leakage.

[0047] Generally, the greater the depth of the formation, the higher the static temperature and pressure of the formation. Initially, the static pressure equals the initial pressure in the formation before production. After production begins, the static pressure approaches the average reservoir pressure.

[0048] A "design" refers to the estimate or measure of one or more parameters planned or expected for a particular fluid or stage of a well service or treatment. For example, a fluid can be designed to have components that provide a minimum density or viscosity for at least a specified time under expected downhole conditions. A well service may include design parameters such as fluid volume to be pumped, required pumping time for a treatment, or the shear conditions of the pumping.

[0049] The term "design temperature" refers to an estimate or measurement of the actual temperature at the downhole environment during the time of a treatment. For example, the design temperature for a well treatment takes into account not only the bottom hole static temperature ("BHST"), but also the effect of the temperature of the fluid on the BHST during treatment. The design temperature for a fluid is sometimes referred to as the bottom hole circulation temperature

("BHCT"). Because fluids may be considerably cooler than BHST, the difference between the two temperatures can be quite large. Ultimately, if left undisturbed a subterranean formation will return to the BHST.

[0050] Physical States and Phases

[0051] As used herein, "phase" is used to refer to a substance having a chemical composition and physical state that is distinguishable from an adjacent phase of a substance having a different chemical composition or different physical state.

[0052] Unless otherwise stated, the physical state or phase of a substance (or mixture of substances) and other physical properties are determined at a temperature of 77° F. (25° C.) and a pressure of 1 atmosphere (Standard Laboratory Conditions) without applied shear.

[0053] Particles and Particulates

[0054] As used herein, a "particle" refers to a body having a finite mass and sufficient cohesion such that it can be considered as an entity but having relatively small dimensions. A particle can be of any size ranging from molecular scale to macroscopic, depending on context.

[0055] A particle can be in any physical state. For example, a particle of a substance in a solid state can be as small as a few molecules on the scale of nanometers up to a large particle on the scale of a few millimeters, such as large grains of sand. Similarly, a particle of a substance in a liquid state can be as small as a few molecules on the scale of nanometers up to a large drop on the scale of a few millimeters. A particle of a substance in a gas state is a single atom or molecule that is separated from other atoms or molecules such that intermolecular attractions have relatively little effect on their respective motions.

[0056] As used herein, particulate or particulate material refers to matter in the physical form of distinct particles in a solid or liquid state (which means such an association of a few atoms or molecules). As used herein, a particulate is a grouping of particles having similar chemical composition and particle size ranges anywhere in the range of about 0.5 micrometer (500 nm), for example, microscopic clay particles, to about 3 millimeters, for example, large grains of sand.

[0057] A particulate can be of solid or liquid particles. As used herein, however, unless the context otherwise requires, particulate refers to a solid particulate. Of course, a solid particulate is a particulate of particles that are in the solid physical state, that is, the constituent atoms, ions, or molecules are sufficiently restricted in their relative movement to result in a fixed shape for each of the particles.

[0058] It should be understood that the terms "particle" and "particulate," includes all known shapes of particles including substantially rounded, spherical, oblong, ellipsoid, rod-like, fiber, polyhedral (such as cubic materials), etc., and mixtures thereof. For example, the term "particulate" as used herein is intended to include solid particles having the physical shape of platelets, shavings, flakes, ribbons, rods, strips, spheroids, toroids, pellets, tablets or any other physical shape.

[0059] A particulate will have a particle size distribution ("PSD"). As used herein, "the size" of a particulate can be determined by methods known to persons skilled in the art.

[0060] One way to define the particle size distribution is with values such as d(0.10), d(0.50), or d(0.90). The d(0.50), which is sometimes referred to as the "D50" or the median particle size, is defined as the diameter where half of the particles are smaller and half are larger than the size. Simi-

larly, 10 percent of the distribution lies below the d(0.10) or “D10” size, and 90 percent of the distribution lies below the d(0.90) or “D90” size.

[0061] One way to measure the approximate particle size distribution of a solid particulate is with graded screens. A solid particulate material will pass through some specific mesh (that is, have a maximum size; larger pieces will not fit through this mesh) but will be retained by some specific tighter mesh (that is, a minimum size; pieces smaller than this will pass through the mesh). This type of description establishes a range of particle sizes. A “+” before the mesh size indicates the particles are retained by the sieve, while a “-” before the mesh size indicates the particles pass through the sieve. For example, -70/+140 means that 90% or more of the particles will have mesh sizes between the two values.

[0062] Particulate materials are sometimes described by a single mesh size, for example, 100 U.S. Standard mesh. If not otherwise stated, a reference to a single particle size means about the mid-point of the industry-accepted mesh size range for the particulate.

[0063] Dispersions

[0064] A dispersion is a system in which particles of a substance of one chemical composition and physical state are dispersed in another substance of a different chemical composition or physical state. In addition, phases can be nested. If a substance has more than one phase, the most external phase is referred to as the continuous phase of the substance as a whole, regardless of the number of different internal phases or nested phases.

[0065] A heterogeneous dispersion is a “suspension” where the dispersed particles are larger than about 50 micrometer. Such particles can be seen with a microscope, or if larger than about 50 micrometers (0.05 mm), with the unaided human eye. The dispersed particles of a suspension in a liquid external phase may eventually separate on standing, for example, settle in cases where the particles have a higher density than the liquid phase. Suspensions having a liquid external phase are essentially unstable from a thermodynamic point of view; however, they can be kinetically stable over a long period depending on temperature and other conditions.

[0066] Hydratability or Solubility in Solutions

[0067] As referred to herein, “hydratable” means capable of being hydrated by contacting the hydratable agent with water. Regarding a hydratable agent that includes a polymer, this means, among other things, to associate sites on the polymer with water molecules and to unravel and extend the polymer chain in the water.

[0068] A substance is considered to be “soluble” in a liquid if at least 10 grams of the substance can be hydrated or dissolved in one liter of the liquid when tested at 77° F. and 1 atmosphere pressure for 2 hours, considered to be “insoluble” if less than 1 gram per liter, and considered to be “sparingly soluble” for intermediate solubility values.

[0069] As will be appreciated by a person of skill in the art, the hydratability, dispersibility, or solubility of a substance in water can be dependent on the salinity, pH, or other substances in the water. Accordingly, the salinity, pH, and additive selection of the water can be modified to facilitate the hydratability, dispersibility, or solubility of a substance in aqueous solution. To the extent not specified, the hydratability, dispersibility, or solubility of a substance in water is determined in deionized water, at neutral pH, and without any other additives.

[0070] The “source” of a chemical species in a solution or in a fluid composition can be a material or substance that is itself the chemical species, or that makes the chemical species chemically available immediately, or it can be a material or substance that gradually or later releases the chemical species to become chemically available in the solution or the fluid.

[0071] Fluids

[0072] A fluid can be a single phase or a dispersion. In general, a fluid is an amorphous substance that is or has a continuous phase of particles that are smaller than about 1 micrometer that tends to flow and to conform to the outline of its container.

[0073] As used herein, a fluid is a substance that behaves as a fluid under Standard Laboratory Conditions, that is, at 77° F. (25° C.) temperature and 1 atmosphere pressure, and at the higher temperatures and pressures usually occurring in subterranean formations without any applied shear.

[0074] Every fluid inherently has at least a continuous phase. A fluid can have more than one phase. The continuous phase of a drilling or treatment fluid is a liquid under Standard Laboratory Conditions. For example, a fluid can in the form of be a suspension (solid particles dispersed in a liquid phase), an emulsion (liquid particles dispersed in another liquid phase), or a foam (a gas phase dispersed in liquid phase).

[0075] As used herein, a “water-based” fluid means that water or an aqueous solution is the dominant material of the continuous phase, that is, greater than 50% by weight, of the continuous phase of the fluid based on the combined weight of water and any other solvents in the phase (that is, excluding the weight of any dissolved solids).

[0076] In contrast, an “oil-based” fluid means that oil is the dominant material by weight of the continuous phase of the fluid. In this context, the oil of an oil-based fluid can be any oil.

[0077] In the context of a fluid, oil is understood to refer to any kind of oil in a liquid state, whereas gas is understood to refer to a physical state of a substance, in contrast to a liquid. In this context, an oil is any substance that is liquid under Standard Laboratory Conditions, is hydrophobic, and soluble in organic solvents. Oils typically have a high carbon and hydrogen content and are non-polar substances. This general definition includes classes such as petrochemical oils, vegetable oils, and many organic solvents. All oils, even synthetic oils, can be traced back to organic sources.

[0078] Apparent Viscosity of a Fluid

[0079] Viscosity is a measure of the resistance of a fluid to flow. In everyday terms, viscosity is “thickness” or “internal friction.” Thus, pure water is “thin,” having a relatively low viscosity whereas honey is “thick,” having a relatively higher viscosity. Put simply, the less viscous the fluid is, the greater its ease of movement (fluidity). More precisely, viscosity is defined as the ratio of shear stress to shear rate.

[0080] A Newtonian fluid (named after Isaac Newton) is a fluid for which stress versus strain rate curve is linear and passes through the origin. The constant of proportionality is known as the viscosity. Examples of Newtonian fluids include water and most gases. Newton’s law of viscosity is an approximation that holds for some substances but not others.

[0081] Non-Newtonian fluids exhibit a more complicated relationship between shear stress and velocity gradient (that is, shear rate) than simple linearity. Thus, there exist a number of forms of non-Newtonian fluids. Shear thickening fluids have an apparent viscosity that increases with increasing the rate of shear. Shear thinning fluids have a viscosity that

decreases with increasing rate of shear. Thixotropic fluids become less viscous over time at a constant shear rate. Rheopectic fluids become more viscous over time at a constant shear rate. A Bingham plastic is a material that behaves as a solid at low stresses but flows as a viscous fluid at high stresses.

[0082] Many fluids are non-Newtonian fluids. Accordingly, the apparent viscosity of a fluid applies only under a particular set of conditions including shear stress versus shear rate, which must be specified or understood from the context. In the oilfield and as used herein, unless the context otherwise requires it is understood that a reference to viscosity is actually a reference to an apparent viscosity. Apparent viscosity is commonly expressed in units of centipoise ("cP").

[0083] Like other physical properties, the viscosity of a Newtonian fluid or the apparent viscosity of a non-Newtonian fluid may be highly dependent on the physical conditions, primarily temperature and pressure.

[0084] Gels and Deformation

[0085] The physical state of a gel is formed by a network of interconnected molecules, such as a crosslinked polymer or a network of micelles. The network gives a gel phase its structure and an apparent yield point. At the molecular level, a gel is a dispersion in which both the network of molecules is continuous and the liquid is continuous. A gel is sometimes considered as a single phase.

[0086] Technically, a "gel" is a semi-solid, jelly-like physical state or phase that can have properties ranging from soft and weak to hard and tough. Shearing stresses below a certain finite value fail to produce permanent deformation. The minimum shear stress that will produce permanent deformation is referred to as the shear strength or gel strength of the gel.

[0087] In the oil and gas industry, however, the term "gel" may be used to refer to any fluid having a viscosity-increasing agent, regardless of whether it is a viscous fluid or meets the technical definition for the physical state of a gel. For example, a "base gel" is a term used in the field for a fluid that includes a viscosity-increasing agent, such as guar, but that excludes crosslinking agents. Typically, a base gel is mixed with another fluid containing a crosslinker, wherein the mixture is adapted to form a crosslinked gel. Similarly, a "crosslinked gel" may refer to a substance having a viscosity-increasing agent that is crosslinked, regardless of whether it is a viscous fluid or meets the technical definition for the physical state of a gel.

[0088] Permeability

[0089] Permeability refers to how easily fluids can flow through a material. For example, if the permeability is high, then fluids will flow more easily and more quickly through the material. If the permeability is low, then fluids will flow less easily and more slowly through the material. As used herein, "high permeability" means the material has a permeability of at least 100 milliDarcy (mD). As used herein, "low permeability" means the material has a permeability of less than 1 mD.

[0090] Measurements

[0091] Unless otherwise specified or unless the context otherwise clearly requires, any ratio or percentage means by weight.

[0092] Unless otherwise specified or unless the context otherwise requires, the phrase "by weight of the water" means the weight of the water of the continuous phase of the fluid without the weight of any viscosity-increasing agent, dis-

solved salt, suspended particulate, or other materials or additives that may be present in the water.

[0093] As used herein, "% wt/vol" means the mass-volume percentage, sometimes referred to as weight-volume percentage or percent weight per volume and often abbreviated as % m/v or % w/v, which describes the mass of the solute in g per 100 mL of the liquid. Mass-volume percentage is often used for solutions made from a solid solute dissolved in a liquid. For example, a 40% w/v sugar solution contains 40 g of sugar per 100 mL of liquid.

[0094] Any doubt regarding whether units are in U.S. or Imperial units, where there is any difference, U.S. units are intended. For example, "gal/Mgal" means U.S. gallons per thousand U.S. gallons.

[0095] The micrometer (μm) may sometimes referred to herein as a micron.

[0096] Unless otherwise stated, mesh sizes are in U.S. Standard Mesh.

General Objective

[0097] The invention provides compositions and methods for degrading an aliphatic polyester, such as a polylactide, which can be used, for example, in well treatments such as fluid-loss control or diversion of fluids in a well. The compositions and methods related to degrading a polylactide particulate deposited in a well.

[0098] To reduce time of shut-in and well costs for the jobs involve polylactide material, an alkali solution (such as aqueous NaOH) with small concentration of an oxidative breaker (such as sodium chlorite or tert-butyl hydrogen peroxide) can quickly degrade an aliphatic polyester such as a polylactide.

[0099] Methods of treating a portion of a well are provided, the methods including the steps of: (A) depositing a solid particulate into the portion of the well, wherein the solid particulate comprises an aliphatic polyester; and (B) contacting the particulate with a treatment fluid comprising: (i) water; (ii) a source of a strong alkali; and (iii) a source of a strong oxidizer. The steps of depositing and contacting can be with a single treatment fluid or separate treatment fluids.

[0100] In an embodiment of the invention, a method of treating a portion of a well includes the step of: introducing a treatment fluid into the portion of the well, wherein the treatment fluid comprises: (i) a solid particulate, wherein the solid particulate is deposited in the well, and wherein the solid particulate comprises an aliphatic polyester; (ii) water; (iii) a source of a strong alkali; and (iv) a source of a strong oxidizer.

[0101] In another embodiment, a method of treating a portion of a well includes the steps of: (A) introducing a first treatment fluid into the portion of the well, wherein the first treatment fluid comprises a solid particulate, wherein the solid particulate is deposited in the well, and wherein the solid particulate comprises an aliphatic polyester; and (B) before or after the step of introducing the first treatment fluid into the portion of the well, introducing a second treatment fluid into the portion of the well, whereby the second treatment fluid contacts the solid particulate in the portion of the well, and wherein the second treatment fluid comprises: (i) water; (ii) a source of a strong alkali; and (iii) a source of a strong oxidizer.

Degradable Solid Particulate

[0102] As used herein, a "degradable" solid material is capable of undergoing an irreversible degradation downhole. The term "irreversible" as used herein means that the degrad-

able material once degraded should not recrystallize or reconsolidate while downhole in the treatment zone, that is, the degradable material should degrade in situ but should not recrystallize or reconsolidate in situ.

[0103] The terms “degradable” or “degradation” refer to both the two relatively extreme cases of degradation that the degradable material may undergo, that is, heterogeneous (or bulk erosion) and homogeneous (or surface erosion), and any stage of degradation in between these two.

[0104] The degradation can be a result of a chemical or thermal reaction or a reaction induced by radiation. The degradable material is preferably selected to degrade by at least one mechanism selected from the group consisting of: hydrolysis, hydration followed by dissolution, dissolution, decomposition, or sublimation.

[0105] In general, selection of a degradable material and treatment fluid depends on a number of factors including: (1) the degradability of the material; (2) the particle size of the degradable material; (3) the pH of the treatment fluid, if water-based; (4) the design temperature; and (5) the loading of degradable material in the treatment fluid.

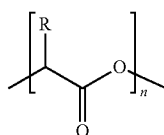
[0106] The choice of degradable material can depend, at least in part, on the conditions of the well, for example, a design temperature during a treatment.

[0107] In choosing the appropriate degradable material, the degradation products that will result should also be considered. For example, the degradation products should not adversely affect other operations or components in the well.

[0108] It is to be understood that a degradable material can include mixtures of two or more different degradable compounds.

[0109] The degradable material used according to the present invention comprises or is an aliphatic polyester. Such polyesters may be linear, graft, branched, crosslinked, block, dendritic, homopolymers, random, block, and star- and hyper-branched aliphatic polyesters, etc.

[0110] Aliphatic polyesters degrade chemically, including by hydrolytic cleavage. Hydrolysis can be catalyzed by acids, bases, enzymes, or metal salt catalyst solutions. Generally, during the hydrolysis, carboxylic end groups are formed during chain scission, and this may enhance the rate of further hydrolysis. This mechanism is known in the art as “autocatalysis,” and is thought to make polyester matrices more bulk eroding. Suitable aliphatic polyesters have the general formula of repeating units shown below:



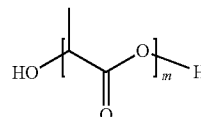
Formula I

where n is an integer above 75 and more preferably between 75 and 10,000 and R is selected from the group consisting of hydrogen, alkyl, aryl, alkylaryl, acetyl, heteroatoms, and mixtures thereof.

[0111] Of the suitable aliphatic polyesters, poly(lactide) is preferred. Poly(lactide) is synthesized either from lactic acid by a condensation reaction or more commonly by ring-opening polymerization of cyclic lactide monomer. Since both lactic acid and lactide can achieve the same repeating unit, the general term poly(lactic acid) as used herein refers to formula

I without any limitation as to how the polymer was made such as from lactides, lactic acid, or oligomers, and without reference to the degree of polymerization or level of plasticization.

[0112] The lactide monomer exists generally in three different forms: two stereoisomers L- and D-lactide and racemic D,L-lactide (meso-lactide). The oligomers of lactic acid and oligomers of lactide are defined by the formula:



Formula II

where m is an integer $2 \leq m \leq 75$. Preferably m is an integer and $2 \leq m \leq 10$. These limits correspond to number average molecular weights below about 5,400 and below about 720, respectively. The chirality of the lactide units provides a means to adjust, among other things, degradation rates, as well as physical and mechanical properties. Poly(L-lactide), for instance, is a semicrystalline polymer with a relatively slow hydrolysis rate. This could be desirable in applications where a slower degradation of the degradable material is desired. Poly(D,L-lactide) may be a more amorphous polymer with a resultant faster hydrolysis rate. This may be suitable for other applications where a more rapid degradation may be appropriate. The stereoisomers of lactic acid may be used individually or combined.

[0113] Additionally, lactide monomers can be copolymerized with, for example, glycolide or other monomers like ϵ -caprolactone, 1,5-dioxepan-2-one, trimethylene carbonate, or other suitable monomers to obtain polymers with different properties or degradation times.

[0114] Additionally, the lactic acid stereoisomers can be modified to be used by, among other things, blending, copolymerizing or otherwise mixing the stereoisomers, blending, copolymerizing or otherwise mixing high and low molecular weight polylactides, or by blending, copolymerizing or otherwise mixing a polylactide with another polyester or polyesters. See U.S. application Publication Nos. 2005/0205265 and 2006/0065397, incorporated herein by reference. One skilled in the art would recognize the utility of oligomers of other organic acids that are polyesters.

[0115] The size of the degradable polymer depends on the specific application and purpose of the particulate. Preferably or in an embodiment, the degradable polymer particulate has a particle size in the range of about 0.005 millimeter (5 micron) to about 5 millimeter. More preferably, the degradable particulate has a particle size in the range of about 0.020 millimeter (20 micron) to about 2 millimeter.

[0116] It should be understood that the degradable polymer is of insufficient particle strengths and other properties for use as a proppant in hydraulic fracturing.

[0117] Preferably or in an embodiment, the solid particulate consists essentially of one or more polylactides.

[0118] One suitable commercially available particulate comprises 90 to 100% polylactide and has a specific gravity of about 1.25. It is commonly available in 150 mesh and 320 mesh.

[0119] For example, a degradable solid particulate can be added to a drilling or treatment fluid in an amount necessary to give the desired fluid-loss control. In some embodiments,

the polylactide particulate can be included in an amount of about 5 to about 200 lbs/Mgal of the fluid. In some embodiments, the polylactide particulate can be included in an amount from about 10 to about 50 lbs/Mgal of the fluid.

Treatment Fluids Preferably Water-Based

[0120] A drilling or treatment fluid adapted for carrying and depositing the solid particulate into a portion of the well is preferably water-based. Similarly, a treatment fluid adapted for degrading the solid particulate is preferably water-based. The fluids for these two purposes can be combined or separate, depending, for example, on the timing desired for degrading the solid particulate.

[0121] Preferably, the water is present in the treatment fluids in an amount at least sufficient to substantially hydrate any viscosity-increasing agent. In some embodiments, the aqueous phase, including the dissolved materials therein, may be present in the treatment fluids in an amount in the range from about 5% to 100% by volume of the treatment fluid.

[0122] Preferably, the water for use in a drilling or treatment fluid does not contain anything that would adversely interact with the other components used in the fluid or with the subterranean formation.

[0123] The aqueous phase can include freshwater or non-freshwater. Non-freshwater sources of water can include surface water ranging from brackish water to seawater, brine, returned water (sometimes referred to as flowback water) from the delivery of a fluid into a well, unused fluid, and produced water. As used herein, brine refers to water having at least 40,000 mg/L total dissolved solids.

[0124] In some embodiments, the aqueous phase of the treatment fluid may comprise a brine. The brine chosen should be compatible with the formation and should have a sufficient density to provide the appropriate degree of well control.

[0125] Salts may optionally be included in the treatment fluids for many purposes. For example, salts may be added to a water source, for example, to provide a brine, and a resulting treatment fluid, having a desired density. Salts may optionally be included for reasons related to compatibility of the treatment fluid with the formation and formation fluids. To determine whether a salt may be beneficially used for compatibility purposes, a compatibility test may be performed to identify potential compatibility problems. From such tests, one of ordinary skill in the art with the benefit of this disclosure will be able to determine whether a salt should be included in a treatment fluid.

[0126] Suitable salts can include, but are not limited to, calcium chloride, sodium chloride, magnesium chloride, potassium chloride, sodium bromide, potassium bromide, ammonium chloride, sodium formate, potassium formate, cesium formate, mixtures thereof, and the like. The amount of salt that should be added should be the amount necessary for formation compatibility, such as stability of clay minerals, taking into consideration the crystallization temperature of the brine, for example, the temperature at which the salt precipitates from the brine as the temperature drops.

Viscosity of Treatment Fluid for Carrying a Particulate

[0127] A drilling or treatment fluid can be adapted to be a carrier fluid for one or more particulates, such as a particulate comprising an aliphatic polyester to be deposited into a treatment zone of a well.

[0128] As many fluids used in wells are water-based, partly for the purpose of helping to suspend particulate of higher density, and for other reasons known in the art, the density of the fluid used in a well can be increased by including highly water-soluble salts in the water, such as potassium chloride. However, increasing the density of a fluid will rarely be sufficient to match the density of the particulate.

[0129] Increasing the viscosity of a fluid can help prevent a particulate having a different specific gravity than the liquid phase in which it is dispersed from quickly separating out of the liquid phase.

[0130] A viscosity-increasing agent can be used to increase the ability of a fluid to suspend and carry a particulate material in a fluid. A viscosity-increasing agent can be used for other purposes, such as matrix diversion, conformance control, or friction reduction.

[0131] A viscosity-increasing agent is sometimes referred to in the art as a viscosifying agent, viscosifier, thickener, gelling agent, or suspending agent. In general, any of these refers to an agent that includes at least the characteristic of increasing the viscosity of a fluid in which it is dispersed or dissolved. There are several kinds of viscosity-increasing agents and related techniques for increasing the viscosity of a fluid.

[0132] In general, because of the high volume of fracturing fluid typically used in a fracturing operation, it is desirable to efficiently increase the viscosity of fracturing fluids to the desired viscosity using as little viscosity-increasing agent as possible. In addition, relatively inexpensive materials are preferred. Being able to use only a small concentration of the viscosity-increasing agent requires a lesser amount of the viscosity-increasing agent in order to achieve the desired fluid viscosity in a large volume of fracturing fluid.

[0133] Polymers for Increasing Viscosity

[0134] Certain kinds of polymers can be used to increase the viscosity of a fluid. In general, the purpose of using a polymer is to increase the ability of the fluid to suspend and carry a particulate material. Polymers for increasing the viscosity of a fluid are preferably soluble in the external phase of a fluid. Polymers for increasing the viscosity of a fluid can be naturally occurring polymers such as polysaccharides, derivatives of naturally occurring polymers, or synthetic polymers.

[0135] Treatment fluids used in high volumes, such as fracturing fluids, are usually water-based. Efficient and inexpensive viscosity-increasing agents for water include certain classes of water-soluble polymers.

[0136] As will be appreciated by a person of skill in the art, the dispersibility or solubility in water of a certain kind of polymeric material may be dependent on the salinity or pH of the water. Accordingly, the salinity or pH of the water can be modified to facilitate the dispersibility or solubility of the water-soluble polymer. In some cases, the water-soluble polymer can be mixed with a surfactant to facilitate its dispersibility or solubility in the water or salt solution utilized.

[0137] The water-soluble polymer can have an average molecular weight in the range of from about 50,000 to 20,000,000, most preferably from about 100,000 to about 4,000,000. For example, guar polymer is believed to have a molecular weight in the range of about 2 to about 4 million.

[0138] Typical water-soluble polymers used in well treatments include water-soluble polysaccharides and water-soluble synthetic polymers (for example, polyacrylamide).

The most common water-soluble polysaccharides employed in well treatments are guar and its derivatives.

[0139] As used herein, a “polysaccharide” can broadly include a modified or derivative polysaccharide. As used herein, “modified” or “derivative” means a compound or substance formed by a chemical process from a parent compound or substance, wherein the chemical skeleton of the parent is retained in the derivative. The chemical process preferably includes at most a few chemical reaction steps, and more preferably only one or two chemical reaction steps. As used herein, a “chemical reaction step” is a chemical reaction between two chemical reactant species to produce at least one chemically different species from the reactants (regardless of the number of transient chemical species that may be formed during the reaction). An example of a chemical step is a substitution reaction. Substitution on a polymeric material may be partial or complete.

[0140] A polymer can be classified as being single chain or multi chain, based on its solution structure in aqueous liquid media. Examples of single-chain polysaccharides that are commonly used in the oilfield industry include guar, guar derivatives, and cellulose derivatives. Guar polymer, which is derived from the beans of a guar plant, is referred to chemically as a galactomannan gum. Examples of multi-chain polysaccharides include xanthan, diutan, and scleroglucan, and derivatives of any of these. Without being limited by any theory, it is currently believed that the multi-chain polysaccharides have a solution structure similar to a helix or are otherwise intertwined.

[0141] Because such fluids have high viscosity under low shear conditions, it can be useful to suspend particulates similar to a fluid viscosified with a cross-linked polymer. In addition, the high viscosities under low shear attained with these polymer loadings can be used to help control fluid losses during workover and completion operations with reduced damage to the formation.

[0142] The viscosity-increasing agent can be provided in any form that is suitable for the particular treatment fluid or application. For example, the viscosity-increasing agent can be provided as a liquid, gel, suspension, or solid additive that is admixed or incorporated into a treatment fluid.

[0143] The viscosity-increasing agent should be present in a treatment fluid in a form and in an amount at least sufficient to impart the desired viscosity to a treatment fluid. For example, the amount of viscosity-increasing agent used in the treatment fluids may vary from about 0.25 pounds per 1,000 gallons of treatment fluid (“lbs/Mgal”) to about 200 lbs/Mgal. In other embodiments, the amount of viscosity-increasing agent included in the treatment fluids may vary from about 10 lbs/Mgal to about 80 lbs/Mgal. In another embodiment, about 20 pounds to about 70 pounds (lbs) of water-soluble polymer per 1,000 gallons (Mgal) of water (equivalent to about 2.4 g/L to about 8.4 g/L).

[0144] Crosslinking of Polymer to Increase Viscosity of a Fluid or Form a Gel

[0145] The viscosity of a fluid at a given concentration of viscosity-increasing agent can be greatly increased by crosslinking the viscosity-increasing agent. A crosslinking agent, sometimes referred to as a crosslinker, can be used for this purpose. A crosslinker interacts with at least two polymer molecules to form a “crosslink” between them.

[0146] If crosslinked to a sufficient extent, the polysaccharide may form a gel with water. Gel formation is based on a number of factors including the particular polymer and con-

centration thereof, the particular crosslinker and concentration thereof, the degree of crosslinking, temperature, and a variety of other factors known to those of ordinary skill in the art.

[0147] Sometimes, however, crosslinking is undesirable, as it may cause the polymeric material to be more difficult to break and it may leave an undesirable residue in the formation.

[0148] Viscosifying Surfactants (that is Viscoelastic Surfactants)

[0149] It should be understood that merely increasing the viscosity of a fluid may only slow the settling or separation of distinct phases and does not necessarily stabilize the suspension of any particles in the fluid.

[0150] Certain viscosity-increasing agents can also help suspend a particulate material by increasing the elastic modulus of the fluid. The elastic modulus is the measure of a substance’s tendency to be deformed non-permanently when a force is applied to it. The elastic modulus of a fluid, commonly referred to as G' , is a mathematical expression and defined as the slope of a stress versus strain curve in the elastic deformation region. G' is expressed in units of pressure, for example, Pa (Pascals) or dynes/cm². As a point of reference, the elastic modulus of water is negligible and considered to be zero.

[0151] An example of a viscosity-increasing agent that is also capable of increasing the suspending capacity of a fluid is to use a viscoelastic surfactant. As used herein, the term “viscoelastic surfactant” refers to a surfactant that imparts or is capable of imparting viscoelastic behavior to a fluid due, at least in part, to the association of surfactant molecules to form viscosifying micelles.

[0152] Viscoelastic surfactants may be cationic, anionic, or amphoteric in nature. The viscoelastic surfactants can comprise any number of different compounds, including methyl ester sulfonates, hydrolyzed keratin, sulfosuccinates, taurates, amine oxides, ethoxylated amides, alkoxyated fatty acids, alkoxyated alcohols (for example, lauryl alcohol ethoxylate, ethoxylated nonyl phenol), ethoxylated fatty amines, ethoxylated alkyl amines (for example, cocoalkylamine ethoxylate), betaines, modified betaines, alkylamido-betaines (for example, cocoamidopropyl betaine), quaternary ammonium compounds (for example, trimethyltallowammonium chloride, trimethylcocoammonium chloride), derivatives thereof, and combinations thereof.

[0153] Breaker for Viscosity of Fluid

[0154] After a treatment fluid is placed where desired in the well and for the desired time, the fluid usually must be removed from the wellbore or the formation. For example, in the case of hydraulic fracturing, the fluid should be removed leaving the proppant in the fracture and without damaging the conductivity of the proppant bed. To accomplish this removal, the viscosity of the treatment fluid must be reduced to a very low viscosity, preferably near the viscosity of water, for optimal removal from the propped fracture. Similarly, when a viscosified fluid is used for gravel packing, the viscosified fluid must be removed from the gravel pack.

[0155] Reducing the viscosity of a viscosified treatment fluid is referred to as “breaking” the fluid. Chemicals used to reduce the viscosity of fluids are called breakers.

[0156] No particular mechanism is necessarily implied by the term. For example, a breaker can reverse the crosslinking. In another approach, a breaker can reduce the molecular weight of a water-soluble polymer by cutting the long poly-

mer chain. As the length of the polymer chain is cut, the viscosity of the fluid is reduced. For instance, reducing the guar polymer molecular weight to shorter chains having a molecular weight of about 10,000 converts the fluid to near water-thin viscosity. This process can occur independently of any crosslinking bonds existing between polymer chains.

Alkali and Oxidizer for Degrading Solid Polyester Material

[0157] As discussed above, a treatment fluid adapted for degrading the solid particulate is preferably water-based.

[0158] As used herein, an alkali is a basic, ionic salt of an alkali metal or alkaline earth metal element. An alkali solution is an aqueous solution of an alkali.

[0159] Preferably or in an embodiment, the source of the strong alkali is selected from the group consisting of: an alkali metal hydroxide, an alkaline earth metal hydroxide, an alkaline earth oxide, and any combination thereof. The source of the strong alkali forms an alkali solution.

[0160] Preferably or in an embodiment, the source of the strong alkali is in the range of about 0.5% to about 20% by weight of the water of the treatment fluid.

[0161] Preferably or in an embodiment, the source of the strong alkali is in at least a sufficient concentration such that the pH of the water of the treatment fluid is at least 12.

[0162] An oxidizer, also commonly referred to as an oxidant or oxidizing agent, is a substance that oxidizes (removes electrons from) another reactant in a redox chemical reaction. An oxidizer is reduced by taking electrons onto itself and the reactant is oxidized by having its electrons taken away. Oxygen is the prime example among the varied types of oxidizing agents.

[0163] Preferably or in an embodiment, the oxidizer is a strong oxidizer.

[0164] For example, the source of the oxidizer can be selected from the group consisting of: chemicals that can release or that contain hydrogen peroxide, chemicals that can release or contain chlorite, and any combination thereof. Presently most preferred oxidizers are selected from the group consisting of chlorites (such as sodium chlorite) and tert-butyl hydrogen peroxide ("TBHP").

[0165] Preferably or in an embodiment, the source of the oxidizer is in the range of about 0.1% to about 15% by weight of the water of the treatment fluid. For a chlorite, a more preferred range is 0.5% to 5% by weight of the water. For TBHP, a more preferred range is 2% to 5% by weight of the water.

Other Fluid Additives

[0166] In certain embodiments, a fluid for use according to the invention can optionally comprise other commonly used fluid additives, such as those selected from the group consisting of surfactants, bactericides, other fluid-loss control additives, stabilizers, chelating agents, scale inhibitors, corrosion inhibitors, hydrate inhibitors, clay stabilizers, salt substitutes (such as trimethyl ammonium chloride), relative permeability modifiers (such as HPT-1™ commercially available from Halliburton Energy Services, Duncan, Okla.), sulfide scavengers, fibers, nanoparticles, and any combinations thereof.

Treatment Methods

[0167] Forming a Drilling or Treatment Fluid

[0168] A fluid can be prepared at the job site, prepared at a plant or facility prior to use, or certain components of the fluid

can be pre-mixed prior to use and then transported to the job site. Certain components of the fluid may be provided as a "dry mix" to be combined with fluid or other components prior to or during introducing the fluid into the well.

[0169] In certain embodiments, the preparation of a fluid can be done at the job site in a method characterized as being performed "on the fly." The term "on-the-fly" is used herein to include methods of combining two or more components wherein a flowing stream of one element is continuously introduced into flowing stream of another component so that the streams are combined and mixed while continuing to flow as a single stream as part of the on-going treatment. Such mixing can also be described as "real-time" mixing.

[0170] Introducing Fluid into Well or Zone

[0171] Often the step of delivering a fluid into a well is within a relatively short period after forming the fluid, for example, less within 30 minutes to one hour. More preferably, the step of delivering the fluid is immediately after the step of forming the fluid, which is "on the fly."

[0172] It should be understood that the step of delivering a fluid into a well can advantageously include the use of one or more fluid pumps.

[0173] In an embodiment, the step of introducing is at a rate and pressure below the fracture pressure of the treatment zone.

[0174] In an embodiment, the step of introducing comprises introducing under conditions for fracturing a treatment zone. The fluid is introduced into the treatment zone at a rate and pressure that are at least sufficient to create or extend at least one fracture in the zone.

[0175] Design Temperature, Time for Degrading, and Flow Back

[0176] After the step of introducing a fluid comprising a degradable material, the methods can include a step of allowing degradable materials to degrade. This preferably occurs with time under the conditions in the zone of the subterranean fluid. It is contemplated, however, that a clean-up treatment could be introduced into the zone to help degrade the degradable material.

[0177] According to the invention, the time for degrading the solid particulate of an aliphatic ester can be very short, even at relative low temperatures of less than about 93° C. (200° F.). For example, while the methods can be used at higher design temperatures, the time for degrading can be adapted to be less than 1 hour even at a lower design temperature in the range of about 20° C. (68° F.) to about 93 (200° F.). More preferably, the time for degrading can be adapted to be less than 30 minutes at such temperatures, which would mean that fluid could be flowed back about immediately after a treatment with a treatment fluid adapted to degrade the solid particulate of an aliphatic ester such as a polylactide. Of course, a limiting factor on a higher design temperature would be the melting point of the material for the solid particulate.

[0178] After the solid particulate is sufficiently degraded, fluid can be flowed back from the treatment zone.

[0179] Producing Hydrocarbon from Subterranean Formation

[0180] Preferably, after any such well treatment, a step of producing hydrocarbon from the subterranean formation is the desirable objective.

EXAMPLES

[0181] To facilitate a better understanding of the present invention, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the entire scope of the invention.

[0182] To demonstrate the efficacy of fluids according to the invention for degrading solid polylactide particulate, example fluids of alkali solutions with different strong oxidizers were prepared and tested.

[0183] The fluids were 10% sodium hydroxide solutions; however, it is believed the lower or higher concentrations of an alkali would be effective.

[0184] The oxidizers were either sodium chlorite (10% aq.) or tert-butyl hydrogen peroxide ("TBHP") (10% aq.) mixed to provide the oxidizer in the stated percentage by weight of the water.

[0185] The polylactide material used in the examples was a particulate having a D50 in the range 325 to 425 micron.

[0186] In the tests, 0.4% w/v of the polylactide particulate was added to a reference of water or the example fluids for comparison.

[0187] Tables 1 and 2 and the FIGS. 1 and 2 show the results and analysis on polylactide degradation (in % by weight) in water or an aqueous NaOH solution with small concentrations of TBHP (solid) or sodium chlorite (10% aq.).

TABLE 1

Polylactide Degradation (% by weight) at 27° C. (80° F.)			
Time (min)	In Water	In Aqueous Alkali Solution (10% NaOH) + 1.6% w/w Sodium Chlorite	In 10% NaOH + 2.4% w/w TBHP
0	9.22	31.45	17.74
30	15	41.65	44.4

TABLE 2

Polylactide Degradation (% by weight) at 93° C. (200° F.)			
Time (min)	In Aqueous Alkali Solution (10% NaOH) + 1.6% w/w Sodium Chlorite	In 10% NaOH + 2.4% w/w TBHP	
0	48.54	49.63	
30	96.93	94.68	

[0188] FIG. 1 is a graph showing the degradation percentage (x-axis) of polylactide in an alkali treatment fluid with sodium chlorite (square data points) or TBHP (triangular data points) at 200° F. as a function of time in minutes (y-axis).

[0189] FIG. 2 is a graph showing the degradation percentage (x-axis) of polylactide in alkali treatment fluid with sodium chlorite (square data points) or TBHP (triangular data points) at 80° F. as a function of time in minutes (y-axis).

[0190] As can be seen in FIG. 2, polylactide shows a 3 to 4 fold increase in degradation rate compared to water.

[0191] As demonstrated by these examples, polylactide particulate can be substantially degraded and dissolved in less than half-an-hour at or below 93° C. (200° F.) with an aqueous solution of a strong base and an oxidizer.

[0192] Accordingly, polylactide now can be used at low temperature well environments. Larger size polylactide par-

ticulates can be used for plugging natural fractures without worrying about flow back. In addition, immediate flowback is possible; little or no shut-in time required before flowback.

CONCLUSION

[0193] Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein.

[0194] The exemplary fluids disclosed herein may directly or indirectly affect one or more components or pieces of equipment associated with the preparation, delivery, recapture, recycling, reuse, or disposal of the disclosed fluids. For example, the disclosed fluids may directly or indirectly affect one or more mixers, related mixing equipment, mud pits, storage facilities or units, fluid separators, heat exchangers, sensors, gauges, pumps, compressors, and the like used generate, store, monitor, regulate, or recondition the exemplary fluids. The disclosed fluids may also directly or indirectly affect any transport or delivery equipment used to convey the fluids to a well site or downhole such as, for example, any transport vessels, conduits, pipelines, trucks, tubulars, or pipes used to fluidically move the fluids from one location to another, any pumps, compressors, or motors (for example, topside or downhole) used to drive the fluids into motion, any valves or related joints used to regulate the pressure or flow rate of the fluids, and any sensors (that is, pressure and temperature), gauges, or combinations thereof, and the like. The disclosed fluids may also directly or indirectly affect the various downhole equipment and tools that may come into contact with the chemicals/fluids such as, but not limited to, drill string, coiled tubing, drill pipe, drill collars, mud motors, downhole motors or pumps, floats, MWD/LWD tools and related telemetry equipment, drill bits (including roller cone, PDC, natural diamond, hole openers, reamers, and coring bits), sensors or distributed sensors, downhole heat exchangers, valves and corresponding actuation devices, tool seals, packers and other wellbore isolation devices or components, and the like.

[0195] 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. It is, therefore, evident that the particular illustrative embodiments disclosed above may be altered or modified and all such variations are considered within the scope of the present invention.

[0196] The various elements or steps according to the disclosed elements or steps can be combined advantageously or practiced together in various combinations or sub-combinations of elements or sequences of steps to increase the efficiency and benefits that can be obtained from the invention.

[0197] It will be appreciated that one or more of the above embodiments may be combined with one or more of the other embodiments, unless explicitly stated otherwise.

[0198] The invention illustratively disclosed herein suitably may be practiced in the absence of any element or step that is not specifically disclosed or claimed.

[0199] Furthermore, no limitations are intended to the details of construction, composition, design, or steps herein shown, other than as described in the claims.

What is claimed is:

1. A method of treating a portion of a well, the method comprising the step of:

introducing a treatment fluid into the portion of the well, wherein the treatment fluid comprises: (i) a solid particulate, wherein the solid particulate is deposited in the well, and wherein the solid particulate comprises an aliphatic polyester; (ii) water; (iii) a source of a strong alkali; and (iv) a source of a strong oxidizer.

2. The method according to claim 1, wherein the aliphatic polyester is a polylactide.

3. The method according to claim 1, wherein the solid particulate consists essentially of one or more polylactides.

4. The method according to claim 1, wherein the solid particulate has a particulate size distribution anywhere between the range of about 0.005 millimeter to about 5 millimeter.

5. The method according to claim 1, wherein the step of introducing the treatment fluid forms a filtercake in the portion of the well, wherein the filtercake comprises the solid particulate.

6. The method according to claim 1, wherein the treatment fluid comprises a continuous liquid phase that is water-based.

7. The method according to claim 6, wherein the treatment fluid additionally comprises: a viscosity-increasing agent.

8. The method according to claim 7, wherein the treatment fluid additionally comprises: a crosslinker for the viscosity-increasing agent.

9. The method according to claim 1, wherein the source of the strong alkali is in the range of about 1% to about 20% by weight of the water of the treatment fluid.

10. The method according to claim 1, wherein the source of the strong alkali is selected from the group consisting of: an alkali metal hydroxide, an alkaline earth metal hydroxide, an alkaline earth oxide, and any combination thereof.

11. The method according to claim 1, wherein the source of the strong oxidizer is in the range of about 0.5% to about 15% by weight of the water of the treatment fluid.

12. The method according to claim 1, wherein the source of the strong oxidizer is selected from the group consisting of:

chemicals that can release or that contain hydrogen peroxide, chemicals that can release or contain chlorite, and any combination thereof.

13. The method according to claim 1, wherein a design temperature in the portion of well during the method of treating is at most about 93° C. (200° F.).

14. The method according to claim 13, further comprising the step of beginning to flow back a downhole fluid from the portion of the well within about 1 hour of the step of introducing the treatment fluid into the portion of the well.

15. A method of treating a portion of a well, the method comprising the steps of:

(A) introducing a first treatment fluid into the portion of the well, wherein the first treatment fluid comprises a solid particulate, wherein the solid particulate is deposited in the well, and wherein the solid particulate comprises an aliphatic polyester; and

(B) before or after the step of introducing the first treatment fluid into the portion of the well, introducing a second treatment fluid into the portion of the well, whereby the second treatment fluid contacts the solid particulate in the portion of the well, and wherein the second treatment fluid comprises: (i) water; (ii) a source of a strong alkali; and (iii) a source of a strong oxidizer.

16. The method according to claim 15, wherein the first treatment fluid comprises a continuous liquid phase that is water-based.

17. The method according to claim 16, wherein the first treatment fluid additionally comprises: a viscosity-increasing agent.

18. The method according to claim 15, wherein a design temperature in the portion of well during the method of treating is at most about 93° C. (200° F.).

19. The method according to claim 18, further comprising the step of beginning to flow back a downhole fluid from the portion of the well within about 1 hour of the later of the steps of introducing the first treatment fluid or the step of introducing the second treatment fluid into the portion of the well.

* * * * *