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(54) Title: SELF-DEGRADING FIBERS AND ASSOCIATED METHODS OF USE AND MANUFACTURE

(57) Abstract: This invention relates to the use of degradable fibers, and more particularly, to self-degrading fibers and their associated methods of use and manufacture. In one embodiment, the present invention provides a method of treating a portion of a subterranean formation comprising the steps of: providing a treatment fluid comprising a plurality of self-degrading fibers, the self-degrading fibers comprising an outer shell and a core liquid; placing the treatment fluid into a subterranean formation; and treating a portion of the subterranean formation.



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SELF-DEGRADING FIBERS AND ASSOCIATED METHODS OF USE AND MANUFACTURE

BACKGROUND

The present invention relates to the use of degradable fibers, and more particularly, to self-degrading fibers and their associated methods of manufacture and use in subterranean applications.

Degradable materials are increasingly becoming of interest in various subterranean applications based, at least in part, on their ability to degrade or produce desirable degradation products (*e.g.*, acids). One particular degradable material that has received recent attention is poly(lactic acid) ("PLA") because it is a material that will degrade down hole after it has performed a desired function or because its degradation products will perform a desired function (*e.g.*, degrade an acid soluble component).

This invention relates to degradable fibers that may be used in any subterranean application wherein it is desirable to include degradable fibers, for instance, to create voids or produce associated degradation products. Examples of suitable applications include cementing, fracturing, and gravel packing, as well as other applications wherein it may be desirable to produce voids or particular degradation products through the degradation of self-degrading fibers.

Hydraulic cement compositions are commonly utilized in subterranean operations, particularly subterranean well completion and remedial operations. For example, hydraulic cement compositions are used in primary cementing operations whereby pipe strings such as casings and liners are cemented in well bores. Hydraulic cement compositions also are used in remedial cementing operations such as plugging highly permeable zones or fractures in well bores, plugging cracks in holes in pipe strings, and the like. In additional applications, hydraulic cement compositions may be used in fracturing and gravel packing applications to form packs that are similar to gravel packs or proppant packs.

Hydraulic fracturing techniques are commonly used to stimulate subterranean formations to enhance the production of desirable fluids therefrom. In a conventional hydraulic fracturing process, a fracturing fluid is pumped down a well bore and into a fluid-bearing formation. The fracturing fluid is pumped into the formation under a pressure sufficient to create or enlarge fissures in the formation. Fracturing fluids used in conventional hydraulic fracturing techniques include: fresh water, brine, liquid

hydrocarbons, gelled water, or gelled brine. The fracturing fluid may contain a viscosifying or gelling agent to increase its viscosity. The fracturing fluid typically also will contain a proppant that will be deposited in the fractures. Commonly used proppant particulates include particulate materials like sand, walnut shells, glass beads, metal pellets, and ceramic beads. The deposited proppant particulates often form proppant packs in the fractures to help to maintain the integrity of those fractures in the formation.

There have been attempts to use cement compositions as propping agents. Cement compositions are desirable in this application because of their high strength and low cost. In conventional methods, such cement compositions when used as propping agents often contain particulate carbonate salts. In theory, when the carbonate salts are removed from the cement composition at some point before the cement composition develops substantial compressive strength, the resultant cement matrix has some degree of permeability, which allows formation fluids to flow to the well bore. Carbonate salts, however, require an acid to dissolve out of the cement composition. Acid treatment may be unreliable because acid tends to find the path of least resistance within the cement composition, which results in uneven distribution of acid and resultant removal of carbonate salt particulates. Thus, the resultant permeability usually is not sufficient for hydrocarbon production. Moreover, the use of acid undermines the integrity of the cement by destabilizing the structure of the cement matrix, thus weakening the cement strength or consolidation.

Additionally, oil, gas, and water producing wells often are completed in unconsolidated subterranean formations containing loose or incompetent sands that can flow into the well bores with produced fluids. The presence of this sand in the produced fluids is undesirable as it, *inter alia*, may erode equipment, which often substantially increases the costs associated with operating such wells and generally reduces the fluid production capability of the formation. Incompetent subterranean formations include those which contain loose sand that is readily entrained by produced fluids, and those wherein the bonded sand particles comprising the formations lack sufficient bond strength to withstand the forces produced by the intermittent production of fluids from the formations.

Heretofore, unconsolidated formations have been treated by creating fractures in the formations and depositing proppant material, *e.g.*, sand of a selected size, in the fractures to substantially preserve the fractures. In addition, the proppant has heretofore been consolidated within the fractures into hard permeable masses to prevent the proppant from

flowing back and to reduce the migration of sand through the fractures with produced fluids. Further, costly "gravel packs," which may include sand screens, slotted liners, perforated shrouds, and the like, have been utilized in wells to prevent the production of formation sand. In conventional gravel packing operations, graded sand is placed in the annulus between a screen and the walls of the well bore in the producing interval. The resulting structure provides a barrier to migrating sand while allowing desired fluids to flow into the well bore so that they may be produced.

While gravel packs may prevent the production of sand with formation fluids, they often fail and require replacement. This may be due to, for example, the deterioration of the screen as a result of corrosion or the like. The initial installation of a gravel pack adds considerable expense to the cost of completing a well, and the removal and replacement of a failed gravel pack is even more costly.

In horizontal well bores formed in unconsolidated formations, the well bores are often completed open hole, *e.g.*, a casing is not inserted into the well bore. In open hole well bores, oftentimes a slotted liner, sand control screen, gravel pack, or the like is installed into the uncased well bore. This method of completion may be problematic as discussed above in that as the incompetent formation tends to break down as a result of production, the slotted liner, sand control screen, or gravel pack is often bypassed, which may result in formation sand being produced along with formation fluids.

There have been attempts to use a sort of permeable cement in subsurface applications such as gravel packs wherein the permeable cement composition contains a particulate, such as a carbonate salt or oil-soluble resin particulate, that is dissolvable with the addition of a second fluid, *e.g.*, an acid or a hydrocarbon. The thought behind this approach is generally that when the dissolvable particulate dissolves out of the cement mass, voids are left in the cement mass so that the cement mass has some degree of permeability to formation fluids. Such permeable cement compositions and methods, however, have not been successful because the permeability of the cement mass once the particulate is dissolved out has not been satisfactory. This lack of permeability is caused by, *inter alia*, the dissolvable particulate's dependence on contact with a second solvent. Oftentimes, the solvent is not able to interact with a sufficient amount of the dissolvable particulate to adequately dissolve a sufficient amount of the particulate. As a result, not enough of the particulate is dissolved out

of the cement mass to make the cement mass's permeability suitable for subsurface applications such as gravel packing.

SUMMARY

The present invention relates to the use of degradable fibers, and more particularly, to self-degrading fibers and their associated methods of use and manufacture.

In one embodiment, the present invention provides a method of treating a portion of a subterranean formation comprising the steps of: providing a treatment fluid comprising a plurality of self-degrading fibers, the self-degrading fibers comprising an outer shell and a core liquid; placing the treatment fluid into a subterranean formation; and treating a portion of the subterranean formation.

In another embodiment, the present invention provides a method comprising: providing a cement composition that comprises a hydraulic cement, water, and a plurality of self-degrading fibers, the self-degrading fibers comprising an outer shell and a core liquid; placing the cement composition in a subterranean formation; and allowing the cement composition to set therein.

In another embodiment, the present invention provides a method of fracturing a portion of a subterranean formation comprising: providing a fracturing fluid composition that comprises proppant particulates and a plurality of self-degrading fibers, the self-degrading fibers comprising an outer shell and a core liquid; injecting the fracturing fluid into the subterranean formation at a pressure sufficient to create or enhance a fracture in a portion therein; allowing the proppant particulates and self-degrading fibers to conglomerate within the fracture so as to form a permeable proppant matrix therein.

In another embodiment, the present invention provides a method of providing some degree of sand control to a portion of a subterranean formation penetrated by a well bore comprising: providing a gravel pack fluid comprising gravel particulates and a plurality of self-degrading fibers, the self-degrading fibers comprising an outer shell and a core liquid; and placing the gravel pack fluid into the subterranean formation so that a permeable gravel pack forms adjacent to a portion of the subterranean formation.

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

DRAWINGS

The following figures form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these drawings in combination with the description of embodiments presented herein.

Figure 1A depicts one embodiment of a round cross-section of a self-degrading fiber of this invention.

Figure 1B illustrates an embodiment of a trilobal cross-section of a self-degrading fiber of this invention.

Figure 1C illustrates another embodiment of an oval cross-section of a self-degrading fiber of this invention.

Figure 1D illustrates another embodiment of a flat cross-section of a self-degrading fiber of this invention.

Figure 1E illustrates another embodiment of a star cross-section of a self-degrading fiber of this invention.

Figure 1F illustrates another embodiment of a cross-section of a self-degrading fiber of this invention.

DESCRIPTION

The present invention relates to the use of degradable fibers, and more particularly, to self-degrading fibers and their associated methods of use and manufacture. The self-degrading fibers of this invention comprise degradable hollow fibers. Hollow fibers are used widely in various fields.

The self-degrading fibers of this invention may be used in any subterranean application wherein it is desirable for the self-degrading fibers to degrade, *e.g.*, to leave voids, act as a temporary restriction to the flow of a fluid, or produce desirable degradation products. The self-degrading fibers and methods of this invention may be especially beneficial in any application in which the self-degrading fibers will be used does not contain a component that will enable the outer shell of the fibers to degrade, *e.g.*, in a dry gas hole. Moreover, the self-degrading fibers of the present invention are especially suitable for subterranean applications including, but not limited to, cementing (*e.g.*, regular or acid soluble cement compositions), fracturing, or gravel packing applications.

The self-degrading fibers of the present invention comprise an outer shell and a core liquid. The outer shell comprises a degradable polymer, and substantially retains the core liquid. The outer shells of the self-degrading fibers of this invention comprise degradable polymers that are subject to hydrolytic degradation. The core liquids comprise liquids that are able to at least partially facilitate or catalyze the hydrolysis of the degradable polymers in the outer shells. Optionally, the self-degrading fibers of this invention may comprise a coating on the outer shell and/or a suitable additive in the core liquid, *e.g.*, an additive chosen to interact with the degradable polymer, its degradation products, or the surrounding subterranean environment. In preferred embodiments, the outer shell is not porous.

The self-degrading fibers of this invention may have any cross-sectional shape including, but not limited to, round, oval, trilobal, star, flat, rectangular, etc. Figures 1A through 1F illustrate some embodiments of such cross-sections. One should note that certain cross-sectional shapes may allow for varying volumes of core liquids to be included in the fibers. For instance, a round cross-section may allow for a larger volume of a core liquid to be retained within the outer shell, which may be desirable in certain applications when more of the core liquid will be beneficial. One should be mindful that the core liquid should be included in an amount sufficient to allow for hydrolysis of the outer shell of a given self-degrading fiber taking into account all environmental factors. The desired hydrolysis characteristics also will affect the ratio of the outer shell to the core liquid in a particular self-degrading fiber. One guideline that may be helpful in certain applications wherein poly(lactic acid) is included in the outer shell is that about 0.25 grams of water is needed for 1 gram of poly(lactic acid). The particular cross-sectional shape chosen for the self-degrading fibers that will be used in a given application may be dictated, *inter alia*, by the circumstances surrounding the application (*e.g.*, the environmental factors), the desired geometry of any voids that will be created as a result of the degradation of the self-degrading fibers, the time needed to restrict the flow of a fluid, and by the amount of core liquid needed to encourage degradation of the self-degrading fibers. When the self-degrading fibers are used in an application wherein they will degrade to leave voids, one should be mindful that the diameter of the fibers should relate to the size and shape of the voids that will result after degradation of the self-degrading fibers.

Figure 1A depicts one embodiment of a round cross-section of a self-degrading fiber of this invention. Shown generally in Figure 1A are fiber end 104, outer shell 100, and core

liquid 102, which is contained within outer shell 100. Note that outer shell 100 retains core liquid 102 but does not completely enclose it (*i.e.*, fiber end 104 is not closed by the outer shell). In some embodiments, fiber end 104 may be closed if desired.

Figure 1B illustrates an embodiment of a trilobal cross-section of a self-degrading fiber of this invention. Shown generally is fiber end 106, outer shell 108, and core liquid 110. One should note that in some embodiments fiber end 106 may be closed (not pictured in Figure 1B).

Figure 1C illustrates another embodiment of an oval cross-section of a self-degrading fiber of this invention. Shown generally is fiber end 112, outer shell 114, and core liquid 116. One should note that in some embodiments fiber end 112 may be closed (not pictured in Figure 1C).

Figure 1D illustrates another embodiment of a flat cross-section of a self-degrading fiber of this invention. Shown generally is fiber end 118, outer shell 120, and core liquid 122. One should note that in some embodiments fiber end 118 may be closed (not pictured in Figure 1D).

Figure 1E illustrates another embodiment of a star cross-section of a self-degrading fiber of this invention. Shown generally is fiber end 124, outer shell 126, and core liquid 128. One should note that in some embodiments fiber end 124 may be closed (not pictured in Figure 1E).

Figure 1F illustrates another embodiment of a cross-section of a self-degrading fiber of this invention. Shown generally is fiber end 130, outer shell 132, a first core liquid 134 and a second core liquid 136. The first core liquid 134 and the second core liquid 136 may be separated by a barrier 138 that may be any suitable barrier (*e.g.*, a membrane, a portion of the degradable polymer that forms the outer shell, etc.). In these embodiments, the first core liquid and the second core liquid may be chosen so as to interact in a certain way to produce a desired result. For instance, they both may facilitate the degradation of the outer shell or they may react with one another to produce a reaction product that will facilitate the degradation of the degradable polymer in the outer shell. Optionally, one of the core liquids may be chosen so that it facilitates the degradation of the degradable polymer of the outer shell of a self-degrading fiber and the second core liquid may be chosen to perform another function in the application. If desired and practicable, more than two core liquids (*e.g.*, in multiple chambers) may be included inside the self-degrading fibers.

Fiber length, thickness, density, and concentration in a treatment fluid or composition are important variables when choosing the appropriate self-degrading fibers of this invention for a particular application. The self-degrading fibers may have any suitable physical dimensions. The behavior of the self-degrading fibers in a chosen application may be manipulated by manipulating the characteristics of the fibers, such as shape, size, volume of core liquid, etc. Factors to take into account when designing the self-degrading fibers to be used in a particular application include, but are not limited to, the desired geometry of any voids that will be created as a result of the degradation of the self-degrading fibers and the amount of core liquid needed to encourage degradation of the self-degrading fibers. In some embodiments, the self-degrading fibers may have an average or effective diameter of about 2 to about 200 microns, and a length of at least about 1 millimeter. The length of the fibers is limited only by the practical implications of handling, pumping, manufacturing, and the like. In some embodiments, a maximum length for the self-degrading fibers may be about 100 millimeters. An aspect ratio of greater than about 100 may be preferred in some applications. Additionally, the self-degrading fibers may have straight, crimped, curved, spiral-shaped, or other three-dimensional geometries if desired.

The density of the self-degrading fibers may be any suitable density appropriate for a chosen application. In certain embodiments, the density of the fibers should be such that the fibers remain distributed within the treatment fluid or composition in which they are being placed in a subterranean formation. For instance, in some fracturing embodiments, the density of the fibers is preferably about the same as any proppant particulates in the fracturing fluid. In most cases, this will range from about 1 to about 4 g/cm³. Also, for some gravel packing applications, it is preferred that the fibers have a suitable density that will enable them to become incorporated into the resultant gravel pack as desired. In some embodiments, the self-degrading fibers may have a density of about 1 g/cm³.

The concentration of self-degrading fibers in a treatment fluid or composition may vary depending on several factors. One factor is what the desired result is upon degradation of the self-degrading fibers. For instance, if a large percentage of voids are desired, then a larger concentration of self-degrading fibers may be required and vice-versa. Another factor is the ease with which the self-degrading fibers may be placed in a desired location. If it is difficult to place the fibers, a higher concentration may be required to offset this difficulty. Generally, the concentration of self-degrading fibers in a treatment fluid or composition may

be from about 0.01% to about 75% of the treatment fluid or composition. Preferably, the fiber concentration ranges from about 0.1% to about 5% of the treatment fluid or composition.

As used herein, the term "treatment fluid" refers to any fluid that may be used in a subterranean application in conjunction with a desired function and/or for a desired purpose. The term "treatment fluid" does not imply any particular action by the fluid or any component thereof.

Methods of making the self-degrading fibers of this invention include any suitable method for forming hollow fibers. One such method involves extruding hollow fibers made from a desired degradable polymer; soaking the hollow fibers in a liquid that will be the core liquid; saturating the hollow fibers with the liquid; drying the exterior of the outer core of the fibers in such a manner that the liquid is retained in the hollow fibers and becomes a core liquid. Another method involves extruding a spinning solution of a chosen degradable polymer from an annular slit of a double pipe orifice to form a sheath solution while simultaneously, extruding a liquid through the inside pipe of the double pipe orifice to form a core liquid within the hollow fibers. Another method involves using capillary action to place the core liquid in an already formed suitable hollow fiber. Other suitable methods may be used as well.

Nonlimiting examples of degradable polymers that may be used in the self-degrading fibers of the present invention include, but are not limited to, homopolymers, random, block, graft, and star- and hyper-branched aliphatic polyesters. Such suitable polymers may be prepared by polycondensation reactions, ring-opening polymerizations, free radical polymerizations, anionic polymerizations, carbocationic polymerizations, coordinative ring-opening polymerization for, such as, lactones, and any other suitable process. One of the important characteristics of suitable degradable polymers is that they are melt or solution processable. Specific examples of suitable polymers include aliphatic polyesters; poly(lactides); poly(glycolides); poly(ϵ -caprolactones); poly(hydroxybutyrates); polyanhydrides; aliphatic polycarbonates; poly(orthoesters); poly(amides); poly(urethanes); poly(hydroxy ester ethers); and poly(phosphazenes). One guideline for choosing which degradable polymer to use in a particular application is what degradation products will result. The differing molecular structures of the degradable polymers that are suitable for the present invention give a wide range of possibilities regarding regulating the degradation rate of the

degradable polymers. In choosing the appropriate degradable polymer, one should consider the degradation products that will result. For instance, some may form an acid upon degradation; the presence of the acid may be undesirable; others may form degradation products that would be insoluble, and these may be undesirable. Moreover, these degradation products should not adversely affect other operations or components.

The degradability of a polymer depends at least in part on its backbone structure. One of the more common structural characteristics is the presence of hydrolyzable and/or oxidizable linkages in the backbone. The rates of degradation of, for example, polyesters, are dependent on the type of repeat unit, composition, sequence, length, molecular geometry, molecular weight, morphology (*e.g.*, crystallinity, size of spherulites, and orientation), hydrophilicity, surface area, and additives. Also, the environment to which the polymer is subjected may affect how the polymer degrades, *e.g.*, temperature, presence of moisture, oxygen, microorganisms, enzymes, pH, and the like. One of ordinary skill in the art with the benefit of this disclosure will be able to determine what the optimum polymer would be for a given application considering the characteristics of the polymer utilized and the environment to which it will be subjected.

Of these suitable polymers, aliphatic polyesters are preferred. Of the suitable aliphatic polyesters, polyesters of α or β hydroxy acids are preferred. Poly(lactide) is most preferred. Poly(lactide) is synthesized either from lactic acid by a condensation reaction or more commonly by ring-opening polymerization of cyclic lactide monomer. The lactide monomer exists generally in three different forms: two stereoisomers L- and D-lactide and D,L-lactide (*meso*-lactide). The chirality of the lactide units provides a means to adjust, *inter alia*, degradation rates, as well as physical and mechanical properties after the lactide is polymerized. Poly(L-lactide), for instance, is a semicrystalline polymer with a relatively slow hydrolysis rate. This could be desirable in applications of the present invention where slow degradation of the self-degrading fiber is desired. Poly(D,L-lactide) is an amorphous polymer with a much faster hydrolysis rate. This may be suitable for other applications of the methods and compositions of the present invention. The stereoisomers of lactic acid may be used individually or combined for use in the compositions and methods of the present invention. Additionally, they may 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. Additionally,

the lactic acid stereoisomers can be modified by blending high and low molecular weight polylactide or by blending polylactide with other aliphatic polyesters. For example, the degradation rate of the PLA may be affected by blending high and low molecular weight lactide, by using mixture of polylactide and lactide monomer or by blending polylactide with other aliphatic polyesters.

The physical properties of degradable polymers (and, therefore, at least in part, the self-degrading fibers) may depend on several factors such as the composition of the repeat units, flexibility of the chain, presence of polar groups, molecular mass, degree of branching, crystallinity, orientation, etc. For example, short chain branches reduce the degree of crystallinity of polymers while long chain branches lower the melt viscosity and impart, *inter alia*, extensional viscosity with tension-stiffening behavior. The properties of the particular polymer utilized can be further tailored by blending, and copolymerizing it with another polymer, or by a change in the macromolecular architecture (*e.g.*, hyper-branched polymers, star-shaped, or dendrimers, etc.). The properties of any such suitable degradable polymers (such as hydrophilicity, rate of biodegradation, etc.) can be tailored by introducing functional groups along the polymer chains. One of ordinary skill in the art with the benefit of this disclosure will be able to determine the appropriate functional groups to introduce to the polymer chains to achieve the desired effect.

Suitable core liquids include any liquid capable of being held within the outer shell of the self-degrading fibers of this invention. Liquids that may aid the degradation of the degradable polymer of the outer shell are preferred. Such liquids include alcohols, acids, bases and aqueous-based liquids. The core liquid may comprise, for example, fresh water, saltwater (*e.g.*, water containing one or more salts dissolved therein), brine (*e.g.*, saturated salt water), or seawater. The water can be from any source as long as it does not contain an excess of compounds that adversely affect other components in the viscosified treatment fluid. Suitable alcohols include those that are capable of interacting with the degradable polymer such that the degradable polymer degrades (for example through transesterification with the polymer backbone of the degradable polymer). An example of a suitable acid includes glacial acetic acid.

Optionally, the core liquid in an embodiment of the self-degrading fibers of this invention may comprise chosen additives. Such additives may be desirable, for example, to aid in the degradation of the degradable polymer or to retard the degradation of the

degradable polymer. The additive also may be chosen to perform a second function in a well bore. For example, an oxidizer additive may be included in the core liquid that may be used in the well bore, for example, as a breaker. Examples of suitable additives include, but are not limited to, corrosion inhibitors, chelators, enzymes, and breakers.

In additional embodiments, the self-degrading fibers may be coated with a desirable coating. Such coatings may be desirable where it may be beneficial to disperse the self-degrading fibers in a particular fashion within the medium in which the self-degrading fibers are being used, or when it is desirable to alter the degradation rate of the outer shell. A coating also may be desirable when it is preferable to control how the self-degrading fibers consolidate within a matrix (*e.g.*, a proppant matrix or a gravel pack). Any suitable coating that may perform any one of these functions is suitable for use in conjunction with the present invention.

One example of a coating that may be used in conjunction with some embodiments of the self-degrading fibers of the present invention is an adhesive coating. An adhesive coating may be useful, for example, to encourage the fibers to adhere to a substrate (which may be other self-degrading fibers), a portion of a subterranean formation, proppant particulates, gravel particulates, and the like. The adhesive coating may be incorporated with the self-degrading fibers during manufacture or subsequent thereto. The coating may be applied to an entire self-degrading fiber or on any portion thereof. The coating may be sprayed or otherwise applied to the material during the coating process. One form of adhesive which may be used is one that will set over time after the self-degrading fibers have been introduced into a subterranean formation. An alternative adhesive might be one that upon treatment with a catalyst (which is either introduced with the self-degrading fibers into the subterranean formation or prior to or subsequent to addition of the self-degrading fibers to the subterranean formation) whereby the catalyst contacts the adhesive coating within the subterranean formation so as to activate the adhesive.

An example of an additive that may be included in a core liquid and/or coated on a self-degrading fiber that may aid the degradation of the degradable polymer is an enzyme. Protease enzymes have been shown to hasten the hydrolysis or degradation of PLA. Protease enzymes are also known as "proteinases" or "proteinase enzymes." Esterases and lipases may also be suitable for other degradable polymers, like poly(hydroxybutyrates) or , aliphatic polyesters. Typically, these enzymes are isolated from plants, animals, bacteria, and fungi,

and there are very many available commercially. A preferred type of protease enzyme that is useful in the present invention is proteinase K. In certain embodiments of the present invention, the protease enzymes in the enzyme compositions may be spray-dried, freeze-dried, or the like. In certain embodiments, the protease enzymes of the compositions of the present invention may be provided, *inter alia*, in a purified form, in a partially purified form, as whole cells, as whole cell lysates, or any combination thereof. The concentration of the protease enzymes in the core liquid and/or in the coating should be an amount effective to hasten hydrolysis of the degradable polymer in the well bore to a desired degree at given conditions. For instance, if a relatively faster hydrolysis rate is desired, then a higher concentration of the protease enzymes should be included. The actual amount included will depend on, *inter alia*, the temperature of the well bore, the concentration of the degradable polymer, the particular enzyme chosen, and the desired hydrolysis rate.

The self-degrading fibers of this invention may be used in any subterranean application wherein it is desirable for the self-degrading fibers to degrade, *e.g.*, to leave voids, act as a temporary restriction to the flow of a fluid, or produce desirable degradation products. For instance, an example of a method of treating a portion of a subterranean formation comprises: providing a treatment fluid comprising a plurality of self-degrading fibers; placing the treatment fluid into a subterranean formation; and treating a portion of the subterranean formation. The terms "treatment" and "treating" do not imply any particular action with or by the self-degrading fibers or degradation products of the self-degrading fibers of the present invention. Moreover, the self-degrading fibers of the present invention are especially suitable for subterranean applications including, but not limited to, cementing (*e.g.*, regular or acid soluble cement compositions), fracturing, or gravel packing applications.

In some embodiments, the self-degrading fibers of this invention may be used in conjunction with hydraulic cement compositions and their associated applications, including, but not limited to, primary cementing, sand control, and fracturing. In an example of a primary cementing method embodiment, a plurality of self-degrading fibers of this invention may be included in a cement composition that comprises a hydraulic cement, water, and any optional additives. The cement composition can then be used in a primary cementing application in a subterranean operation. An example of such a method comprises the steps of: providing a cement composition that comprises a hydraulic cement, water, and a plurality of self-degrading fibers of this invention; placing the cement composition in the subterranean

formation; and allowing the cement composition to set therein and the self-degrading fibers to degrade. The quantity of self-degrading fibers to include in a cement composition used in a primary cementing operation may range from about 0.01% to about 15% based on the amount of hydraulic cement in the composition. An example of an embodiment of a method is a method comprising: providing a cement composition that comprises a hydraulic cement, water, and a plurality of self-degrading fibers, the self-degrading fibers comprising an outer shell and a core liquid; placing the cement composition in a subterranean formation; and allowing the cement composition to set therein.

The self-degrading fibers of this invention also may be used in a sand control application in a permeable cement composition. An embodiment of a method is a method of providing some degree of sand control to a portion of a subterranean formation penetrated by a well bore comprising: providing a gravel pack fluid comprising gravel particulates and a plurality of self-degrading fibers, the self-degrading fibers comprising an outer shell and a core liquid; and placing the gravel pack fluid into the subterranean formation so that a permeable gravel pack forms adjacent to a portion of the subterranean formation. Another embodiment of providing sand control in a well bore penetrating a subterranean formation comprises the following steps: placing a perforated shroud having perforations, the perforations being sealed by a temporary sealant, in the well bore adjacent to a chosen portion of the subterranean formation; providing a permeable cement composition, the permeable cement composition comprising a hydraulic cement, water, and a plurality of self-degrading fibers; placing the permeable cement composition in an annulus between the perforated shroud and the portion of the subterranean formation; allowing the permeable cement composition to set to form a permeable cement mass in the annulus; and removing the temporary sealant sealing the perforations of the perforated shroud to restore liquid communication between the well bore and the subterranean formation.

The self-degrading fibers may be used in fracturing applications as well, either in conjunction with any suitable fracturing fluid, including a conventional fracturing fluid that comprises a base fluid and a viscosifying agent or a fracturing fluid that comprises a cement composition. One example of these methods of the present invention includes the following steps. A permeable cement composition of the present invention is prepared (either on-the-fly or by a preblending process) that comprises a hydraulic cement, water, and a plurality of self-degrading fibers of this invention. The permeable cement composition is injected into

the subterranean formation at a sufficient pressure to create a fracture in the formation. The permeable cement composition is allowed to set in the fracture, whereby the composition fills and forms a permeable cement matrix therein. After the permeable cement proppant matrix has been formed in the well bore, the well is produced and the permeable cement matrix acts, *inter alia*, to maintain the integrity of the fractures within the formation and allow formation fluids to flow into the well bore. Produced liquids and gases are allowed to flow through the permeable cement matrix, but formation sands in the formation are substantially prevented from passing through the matrix. The self-degrading fibers may be incorporated into the cement composition and become distributed throughout the resultant cement matrix, most preferably uniformly, as the cement matrix forms. After the requisite time period dictated by the characteristics of the self-degrading fibers utilized, the self-degrading fibers are substantially removed from the matrix. As a result, voids are created in the matrix. These voids enhance the permeability of the matrix, which results in, *inter alia*, enhanced fracture conductivity. Enhanced fracture conductivity enhances well productivity, as well productivity is a function of, *inter alia*, fracture conductivity. In certain preferred embodiments, these voids are channel-like and interconnected so that the permeability of the matrix is enhanced.

The self-degrading fibers also may be used in a fracturing operation that does not involve a cement composition to form a proppant pack in a fracture having voids to increase its permeability. An example of such a method of the present invention is a method of increasing the conductivity of a fracture in a subterranean formation that comprises the steps of: providing a fracturing treatment fluid comprising a proppant composition, the proppant composition comprising proppant particulates and a plurality of self-degrading fibers; introducing the proppant composition into the fracture; and allowing the proppant composition to form a proppant matrix having voids in the fracture. In these fracturing methods, any suitable fracturing fluid and any suitable proppant particulates may be used. The fracturing fluid may comprise a base fluid (such as an aqueous fluid) and any suitable viscosifying agent (such as a biopolymer).

The self-degrading fibers also may be incorporated within a gravel pack composition so as to form a gravel pack down hole that has some permeability from the degradation of the self-degrading fibers. In an example of such a method, a gravel pack fluid that comprises gravel and a plurality of self-degrading fibers is placed within a well bore so as to form a

gravel pack therein. The self-degrading fibers are allowed to degrade so that the gravel pack develops some permeability.

In another embodiment, the self-degrading fibers may be incorporated into a gravel pack composition such that when they degrade, they assist in the degradation of a filter cake neighboring the gravel pack. This method is most suited for use with self-degrading fibers that form an acid upon degradation. This acid can be used to degrade an acid-soluble component in the filter cake. An example of such a method of degrading a filter cake in a subterranean formation comprises the steps of: providing a gravel pack composition that comprises gravel particulates and a plurality of self-degrading fibers; placing the gravel pack composition into a subterranean formation so that a gravel pack forms that neighbors a filter cake; allowing the self-degrading fibers to degrade so as to produce an acid; and allowing the acid to contact and degrade a portion of the filter cake. In these sand control methods, any suitable gravel pack composition and any suitable gravel particulates may be used.

Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.

What is claimed is:

1. A method of treating a portion of a subterranean formation comprising the steps of:
 - providing a treatment fluid comprising a plurality of self-degrading fibers, the self-degrading fibers comprising an outer shell and a core liquid;
 - placing the treatment fluid into a subterranean formation; and
 - treating a portion of the subterranean formation.
2. The method of claim 1 wherein at least one of the self-degrading fibers comprises a coating and/or an additive.
3. The method of claim 1 wherein at least one of the self-degrading fibers has at least one of the following: a round cross-sectional shape; an oval cross-sectional shape; a trilobal shape; a star shape; a flat shape; a rectangular shape; a closed fiber end; a diameter of about 2 microns to about 200 microns; a length of at least about 1 millimeter; an aspect ratio of greater than about 100; or a density of about 1 to about 4 g/cm³.
4. The method of claim 1 wherein the concentration of self-degrading fibers in the treatment fluid is about 0.01% to about 75% of the composition of the treatment fluid.
5. The method of claim 1 wherein the outer shell of at least one of the self-degrading fibers comprises at least one of the following: an aliphatic polyester; a poly(lactide); a poly(glycolide); a poly(ϵ -caprolactone); a poly(hydroxybutyrate); a polyanhydride; an aliphatic polycarbonate; a poly(orthoester); a poly(amide); a poly(urethane); a poly(hydroxy ester ether); or a poly(phosphazene).
6. The method of claim 1 wherein the core liquid of at least one of the self-degrading fibers comprises at least one of the following: an alcohol, an acid, a base or an aqueous-based fluid.
7. The method of claim 1 wherein the treatment fluid is a cement composition, a fracturing fluid, or a gravel pack fluid.
8. The method of claim 1 wherein treating the subterranean formation involves a primary cementing operation, placing a permeable cement pack, placing a permeable proppant pack, or placing a gravel pack.
9. The method of claim 1 wherein at least one of the self-degrading fibers has a plurality of core liquids.

10. A method comprising:
 - providing a cement composition that comprises a hydraulic cement, water, and a plurality of self-degrading fibers, the self-degrading fibers comprising an outer shell and a core liquid;
 - placing the cement composition in a subterranean formation; and
 - allowing the cement composition to set therein.
11. The method of claim 10 wherein the outer shell of at least one of the self-degrading fibers comprises at least one of the following: an aliphatic polyester; a poly(lactide); a poly(glycolide); a poly(ϵ -caprolactone); a poly(hydroxybutyrate); a polyanhydride; an aliphatic polycarbonate; a poly(orthoester); a poly(amide); a poly(urethane); a poly(hydroxy ester ether); or a poly(phosphazene).
12. The method of claim 10 wherein at least one of the self-degrading fibers has at least one of the following: a round cross-sectional shape; an oval cross-sectional shape; a trilobal shape; a star shape; a flat shape; a rectangular shape; a closed fiber end; a diameter of about 2 microns to about 200 microns; a length of at least about 1 millimeter; an aspect ratio of greater than about 100; or a density of about 1 to about 4 g/cm³.
13. The method of claim 10 wherein the core liquid of at least one of the self-degrading fibers comprises at least one of the following: an alcohol, an acid, a base or an aqueous-based fluid.
14. A method of fracturing a portion of a subterranean formation comprising:
 - providing a fracturing fluid composition that comprises proppant particulates and a plurality of self-degrading fibers, the self-degrading fibers comprising an outer shell and a core liquid;
 - injecting the fracturing fluid into the subterranean formation at a pressure sufficient to create or enhance a fracture in a portion therein;
 - allowing the proppant particulates and self-degrading fibers to conglomerate within the fracture so as to form a permeable proppant matrix therein.
15. The method of claim 14 wherein the fracturing fluid comprises a hydraulic cement.
16. The method of claim 14 wherein the fracturing fluid comprises a base fluid and a viscosifying agent.

17. The method of claim 14 wherein the outer shell of at least one of the self-degrading fibers comprises at least one of the following: an aliphatic polyester; a poly(lactide); a poly(glycolide); a poly(ϵ -caprolactone); a poly(hydroxybutyrate); a polyanhydride; an aliphatic polycarbonate; a poly(orthoester); a poly(amide); a poly(urethane); a poly(hydroxy ester ether); or a poly(phosphazene).

18. A method of providing some degree of sand control to a portion of a subterranean formation penetrated by a well bore comprising:

providing a gravel pack fluid comprising gravel particulates and a plurality of self-degrading fibers, the self-degrading fibers comprising an outer shell and a core liquid; and

placing the gravel pack fluid into the subterranean formation so that a permeable gravel pack forms adjacent to a portion of the subterranean formation.

19. The method of claim 18 wherein the self-degrading fibers produce an acid upon degradation that is capable of interacting with an acid soluble portion of a filter cake.

20. The method of claim 18 wherein before placing the gravel pack fluid into the subterranean formation, a perforated shroud having perforations is placed into the subterranean formation, the perforations being sealed by a temporary sealant, and the gravel pack fluid is placed between the perforated shroud and the portion of the subterranean formation.

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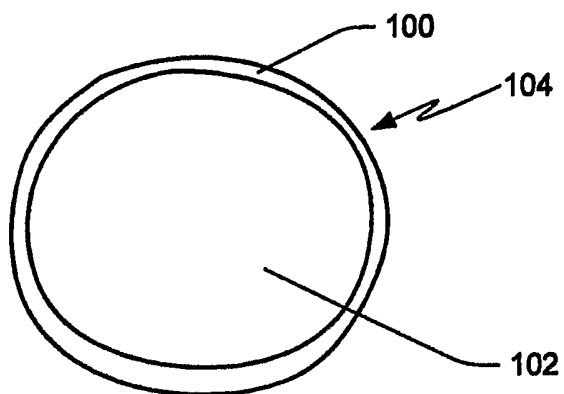


FIG. 1A

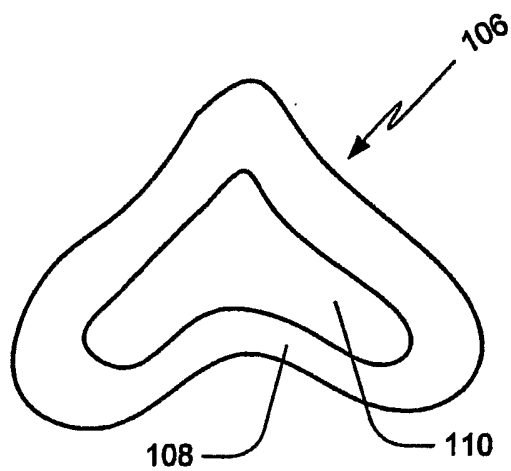


FIG. 1B

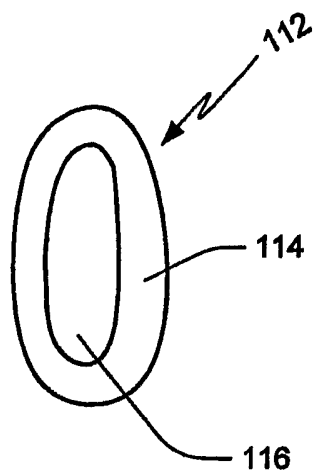


FIG. 1C

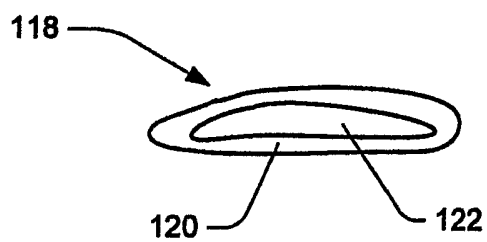


FIG. 1D

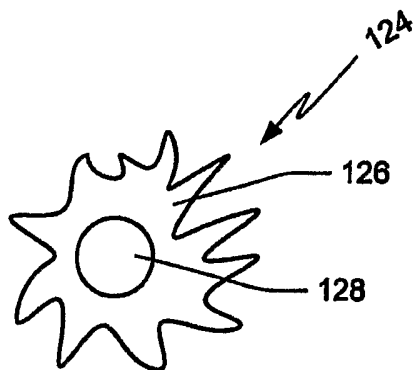


FIG. 1E

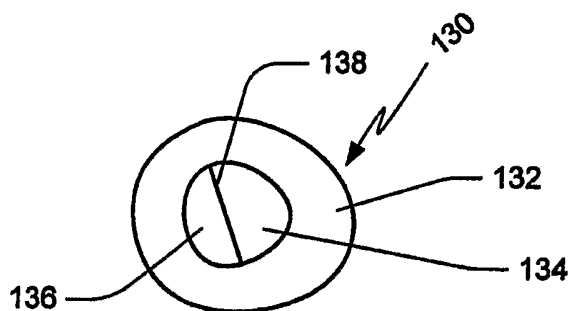


FIG. 1F

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2006/000054

A. CLASSIFICATION OF SUBJECT MATTER

INV. E21B43/04 C09K8/467 C09K8/70

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

E21B C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 439 055 A (CARD ET AL) 8 August 1995 (1995-08-08) claims 11-14 -----	1-9, 14, 16-20
A	US 2004/261996 A1 (MUNOZ TRINIDAD ET AL) 30 December 2004 (2004-12-30) the whole document -----	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

24 May 2006

Date of mailing of the international search report

01/06/2006

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2006/000054

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			DK 619415 T3	21-05-2002
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			US 5330005 A	19-07-1994
US 2004261996	A1	30-12-2004	WO 2005003514 A1	13-01-2005