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(54) **Title:** METHODS FOR SUPPLYING A CHEMICAL WITHIN A SUBTERRANEAN FORMATION

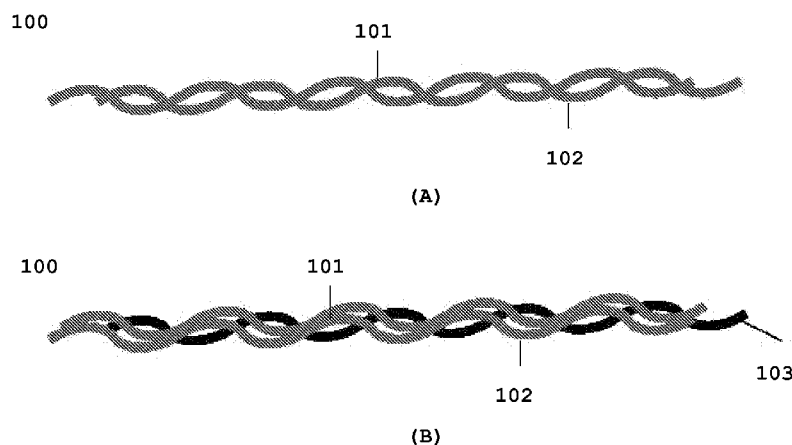


Figure 1

(57) **Abstract:** The method comprises deploying through a well a substantially longitudinal body comprising at least in part a degradable material able to release a chemical; positioning the longitudinal body at a downhole location from the well; and allowing the degradable material to degrade and the chemical to be released.





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Title

METHODS FOR SUPPLYING A CHEMICAL WITHIN A SUBTERRANEAN FORMATION

Field of the Invention

[0001] The invention generally relates to delivering chemicals downhole in a wellbore. Certain types of chemicals are dissolved at a treatment location or close to the treatment location.

Background

[0002] The statements in this section merely provide background information related to the present disclosure and may not constitute prior art.

[0003] In the construction and development of wells formed in subterranean formations, such as wells for the production of oil and gas, various operations are carried out that require the introduction of fluids of different types into the wellbore and/or into formation surrounding the wellbore.

[0004] Certain types of chemicals are preferentially mixed at a treatment location or close to the treatment location. For example, certain mixed chemicals produce strong acids or have highly viscous reaction products, and it may be desirable to minimize equipment contact with the mixed chemicals, or to minimize the operational complexity of mixing and delivering the chemicals. Presently available methods for delivering chemicals directly to a downhole location have drawbacks, including the requirement to prepare for the chemical delivery with special equipment or procedures before the chemical delivery is needed, difficulty in ensuring that the chemicals are delivered to a desired depth, and difficulty in ensuring the chemicals mix at the desired depth. Therefore, further technological developments are desirable in this area.

Summary

[0005] In a first aspect, a method comprises deploying through a well a substantially longitudinal body comprising at least in part a degradable material able to release a chemical; positioning the longitudinal body at a downhole location from the well; and allowing the degradable material to degrade and the chemical to be released.

[0006] In a second aspect, a method comprises deploying with a slickline through a well a substantially longitudinal body attached to the slickline, wherein the longitudinal body comprises at least in part a degradable material able to release a chemical; positioning with the slickline the longitudinal body at a downhole location from the well; and allowing the degradable material to degrade and the chemical to be released.

[0007] In a third aspect, a method comprises adding to a tool selected from the group consisting of slickline, wireline, coil-tubing, micro-coil tubing, and drill string, a substantially longitudinal body comprising at least in part a degradable material; deploying the tool through a well; positioning with the tool the longitudinal body at a downhole location of the well; and allowing the degradable material to degrade and the chemical to be released.

Brief Description of Drawings

[0008] Figure 1 shows an illustration of two embodiments for delivering a chemical to a downhole location in a wellbore.

Detailed Description

[0009] At the outset, it should be noted that in the development of any actual embodiments, numerous implementation-specific decisions must be made to achieve the developer's specific goals, such as compliance with system and business related constraints, which can vary from one implementation to another. Moreover, it will be appreciated that such a development effort might be complex and time consuming but would nevertheless be a routine undertaking for those of ordinary skill in the art having the benefit of this disclosure.

[0010] The description and examples are presented solely for the purpose of illustrating embodiments of the invention and should not be construed as a limitation to the scope and

applicability of the invention. In the summary of the invention and this detailed description, each numerical value should be read once as modified by the term "about" (unless already expressly so modified), and then read again as not so modified unless otherwise indicated in context. Also, in the summary of the invention and this detailed description, it should be understood that a concentration range listed or described as being useful, suitable, or the like, is intended that any and every concentration within the range, including the end points, is to be considered as having been stated. For example, "a range of from 1 to 10" is to be read as indicating each and every possible number along the continuum between about 1 and about 10. Thus, even if specific data points within the range, or even no data points within the range, are explicitly identified or refer to only a few specific, it is to be understood that inventors appreciate and understand that any and all data points within the range are to be considered to have been specified, and that inventors possession of the entire range and all points within the range disclosed and enabled the entire range and all points within the range.

[0011] According to a first embodiment and referring to Figure 1A, a system 100 includes a substantially longitudinal body comprising at least in part a degradable material 101 able to release a chemical. In another embodiment, the system 100 comprises a second degradable material 102 able to release second chemical.

[0012] According to a second embodiment and referring to Figure 1B, the system 100 includes a slickline or wireline 103 and a substantially longitudinal body attached to the slickline, wherein the longitudinal body comprises at least in part a degradable material 101 able to release a chemical. In another embodiment, the system 100 comprises a second degradable material 102 able to release a second chemical. In one embodiment, the degradable material 101 or the second degradable material 102 may comprise a degradable single or a degradable multicore or a degradable hollow core containing a chemical or a reactive fluid.

[0013] According to one embodiment, the first chemical may be used to help to release the second chemical or according to a second embodiment, the first and second chemicals are released independently. According to some further embodiments, the system 100 may comprise a third, fourth or several degradable materials able to release respectively, a third, fourth or several chemicals. The release mechanism can be done by cascade (one chemical

helping to release another chemical) or independently each other or a combination of both. The degradable materials may be the same or different, releasing different chemicals or the degradable materials may be different, releasing same chemical.

[0014] According to some embodiments, the system may be embodied as a system made entirely of degradable material. In one example represented in Figure 1, the system is characterized by helicoidal wires made of degradable materials.

[0015] The degradable material is made of a soluble substrate where the chemical is formed or trapped with the soluble substrate. Under specified conditions including time, temperature, pH values, and/or in the presence of certain solvents (e.g. and without limitation – water, oil, gas, xylene, acetone, or any other solvent understood in the art) the soluble substrate dissolves partially or completely, exposing or releasing the chemical to the surrounding fluid. In certain embodiments, the soluble substrate dissolves over a period of time in the fluids already present (or planned to be present) in the wellbore (e.g. the drilling fluid, hydraulic fracture treatment fluid, gravel pack treatment fluid, etc.), and the release fluid is therefore the fluid already present in the wellbore. According to some embodiments, the degradable material degrades with the help of a release fluid. The release fluid can be any type of chemistry and can be naturally present downhole or can be injected downhole in another step. Examples of release fluid are solvents cited previously.

[0016] Examples of degradable material are material made of degradable fibers or degradable polymers. The differing molecular structures of the degradable materials that are suitable give a wide range of possibilities regarding regulating the degradation rate of the degradable material. 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, fluid flow past the polymer, 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.

[0017] Suitable examples of polymers that may be used include, but are not limited to, homopolymers, random aliphatic polyester copolymers, block aliphatic polyester copolymers, star aliphatic polyester copolymers, or hyperbranched aliphatic polyester copolymers. 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. Specific examples of suitable polymers include polysaccharides such as dextran or cellulose; chitins; chitosans; proteins; aliphatic polyesters; poly(lactides); poly(glycolides); poly(ϵ -caprolactones); poly(hydroxy ester ethers); poly(hydroxybutyrates); polyanhydrides; polycarbonates; poly(orthoesters); poly(acetals); poly(acrylates); poly(alkylacrylates); poly(amino acids); poly(ethylene oxide); poly ether esters; polyester amides; polyamides; polyphosphazenes; and copolymers or blends thereof. Other degradable polymers that are subject to hydrolytic degradation also may be suitable. 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 the 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 where slow degradation of the degradable material is desired. Poly(D,L-lactide) is an amorphous polymer with a much faster hydrolysis rate. 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 polylactic acid may be affected by blending, for example, high and low molecular weight polylactides; mixtures of polylactide and lactide monomer; or by blending polylactide with other aliphatic polyesters.

[0018] One guideline for choosing which composite particles to use in a particular application is what degradation products will result. Another guideline is the conditions surrounding a particular application. In choosing the appropriate degradable material, one should consider the degradation products that will result. For instance, some may form an acid upon degradation, and 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.

[0019] The physical properties of degradable polymers 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 material 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.

[0020] The above mentioned degradable materials in one embodiment are comprised solely of polyester particles, e.g., the system can be free or essentially free of non-polyester solids. In another embodiment, the polyester can be mixed or blended with other degradable or dissolvable solids, for example, solids that react with the hydrolysis products, such as magnesium hydroxide, magnesium carbonate, dolomite (magnesium calcium carbonate), calcium carbonate, aluminum hydroxide, calcium oxalate, calcium phosphate, aluminum metaphosphate, sodium zinc potassium polyphosphate glass, and sodium calcium magnesium polyphosphate glass, for the purpose of increasing the rate of

dissolution and hydrolysis of the degradable material, or for the purpose of providing a supplemental bridging agent that is dissolved by the hydrolysis products. Moreover, examples of reactive solids that can be mixed include ground quartz (or silica flour), oil soluble resins, degradable rock salts, clays such as kaolinite, illite, chlorite, bentonite, or montmorillonite, zeolites such as chabazite, clinoptilolite, heulandite, or any synthetically available zeolite, or mixtures thereof. Degradable materials can also include waxes, oil soluble resins, and other materials that degrade or become soluble when contacted with hydrocarbons.

[0021] The chemical may be any chemical that is desired to be delivered at a downhole location, and may include a polymer cross-linker, a breaker, an acid or an acid precursor, a polyacrylamide, a chemical that contributes to the formation of (or that forms) a fluid loss pill in the surrounding fluid when released, an encapsulated chemical, and/or a coated chemical. Other non-limiting examples of the chemical include sodium hydroxide, fumaric acid, a granular acid, a borate cross-linker, and/or a zirconium cross-linker. The chemical may be in a solid state and, upon release to the surrounding fluid, the chemical may go into solution, become a gas, and/or remain solid. In certain embodiments, the chemical may be found within solid particles in a liquid state, a gas state, and/or an adsorbed material within the solid particles. In certain embodiments, the degradable material when subject to a chemical reaction or a physical transformation may become the chemical. For example, when solid aluminum as degradable material is used, action of acid may release aluminum ions which are the chemicals.

[0022] In one example, the degradable material is aluminum. An aluminum wire or line is used to release aluminum ions downhole. The wire is transformed into soluble aluminum ions by lowering the end of the wire into a solution containing an acid such as hydrochloric acid, hydrofluoric acid, phosphoric acid, or nitric acid. Additional aluminum can be dissolved by feeding the line into the well at the same rate as it dissolves downhole. The aluminum ions act as crosslinking agents and might be needed to effect a crosslink of the solution existing downhole. According to some embodiments, the solution may be a viscosifying agent, for example a polysaccharide such as substituted galactomannans, such as guar gums, high-molecular weight polysaccharides composed of mannose and galactose sugars, or guar derivatives such as hydroxypropyl guar (HPG),

carboxymethylhydroxypropyl guar (CMHPG) and carboxymethyl guar (CMG), hydrophobically modified guar, guar-containing compounds. Also, the viscosifying agent may be a synthetic polymer such as polyvinyl polymers, polymethacrylamides, cellulose ethers, lignosulfonates, and ammonium, alkali metal, and alkaline earth salts thereof. More specific examples of other typical water soluble polymers are acrylic acid-acrylamide copolymers, acrylic acid-methacrylamide copolymers, polyacrylamides, partially hydrolyzed polyacrylamides, partially hydrolyzed polymethacrylamides, polyvinyl alcohol, polyalkyleneoxides, other galactomannans, heteropolysaccharides obtained by the fermentation of starch-derived sugar and ammonium and alkali metal salts thereof. Also, the viscosifying agent may be a cellulose derivative such as hydroxyethylcellulose (HEC) or hydroxypropylcellulose (HPC), carboxymethylhydroxyethylcellulose (CMHEC) and carboxymethylcellulose (CMC). Also, the viscosifying agent may be a biopolymer such as xanthan, diutan, and scleroglucan.

[0023] According to further embodiments, other metal ions can be used as crosslinking agents. Therefore the degradable material may be magnesium, borate, titanium, zirconium, chromium, and antimony, and compositions containing these compounds.

[0024] In another example, the degradable material is a composite material. A line which is made from a composite material is used. The composite material includes a chemical contained within a strong matrix such as plastic. The addition of a solvent downhole will release the chemical from the composite. According to further embodiments, a concentric wire of dissimilar degradable materials that can deploy different chemistries may be used. The inner material being released after the outer material has been degraded.

[0025] Still in another example, the degradable material is soluble at a pH that is significantly different than a treating fluid, and the wellbore is treated with the treating fluid. In the example, where it is desired that the chemical be delivered, the release fluid may be delivered as a slug of treatment fluid having the pH to dissolve the degradable material. In a further example, the chemical may comprise a chemical delivered at the end of a fracture treatment (non-limiting examples of treatment chemicals include a sand control resin, amine based curing agents, fibers (having a chemical composition) that reduce proppant flowback, or a high concentration breaker), and when conditions consistent with delivering the treatment chemical occur (e.g. an imminent screen-out, the

end of the treatment, etc.) then a slug of treatment fluid is delivered to release the chemical.

[0026] In certain embodiments, the release fluid includes a solvent that dissolves the degradable material. In certain embodiments, the release fluid includes a lowered pH, an elevated pH, a solvent, and/or an abrasive. The composition of the release fluid may be variable, according to whether the release fluid is removing or degrading the degradable material.

[0027] Still in another example, the degradable material is a string of poly(lactide) acid (PLA); poly(glycolide) acid (PGA) or a combination of the two that in itself hydrolyzes and generates acid/pH at a specific location and triggers specific chemistry release. A pleated wire/string made of e.g. PLA and PGA that can be temperature triggered may also be realized. PGA for temperature below 225F applications and later trigger PLA at a higher temperature to generate acid.

[0028] In another embodiment, an electrical conductive wire may be used around which PGA and/or PLA wires are wrapped. The conductive wire may be used to generate heat and activate PGA or PLA wires to generate acid if the bottomhole temperature is lower than the natural decomposition temperature for the PLA or PGA.

[0029] A technique for chemical deliver downhole is described. The technique includes an operation to deploy a substantially longitudinal body including a chemical. The technique includes an operation to position the longitudinal body at a downhole location of a well. And the technique includes allowing the chemical to be released. Optionally a release fluid can be used. An operation to flow the release fluid near the longitudinal body may be performed, thereby releasing at least a portion of the chemical into the release fluid.

[0030] In certain embodiments, the operation to release the chemical includes an operation to dissolve the chemical into the release fluid and/or to degrade a degradable material to expose the chemical, and/or a substrate supporting the chemical, to the release fluid. In certain embodiments, the chemical when released will have an exothermic reaction with the second fluid and control the kinetics. The operation to degrade a degradable material includes varying a pH value of the release fluid where the degradable material is responsive to the pH value, including an abrasive material in the release fluid that removes at least part of the degradable material, and/or providing a release fluid wherein the

degradable material is soluble in the release fluid. The operations utilizing the release fluid may include utilizing varying release fluids in multiple steps or stages, including varying pH values, varying temperature values, and/or varying compositions of the release fluid. In one example, an activator that removes the degradable material is included in a part of the release fluid, and the remaining release fluid dissolves the exposed chemical.

[0031] In certain embodiments, the technique includes an operation to provide at least part of the chemical as an encapsulated chemical, and an operation to release the encapsulated chemical into a formation fluidly coupled to the wellbore. In certain embodiments, the technique further includes an operation to form a second degradable material having a second chemical, where the chemical releases in response to a first release operation, and where the second chemical releases in response to a second release operation. In certain embodiments, the technique further includes an operation to form a second degradable material having a second chemical, where the chemical releases in response to a first release operation, and where the second chemical releases in response to the release of said first chemical (cascade mechanism). For example, temperature could be a first operation trigger that releases acid from PLA degradable material. The acid then dissolves aluminum degradable material which release aluminum ions. Or the acid could begin dissolving the wall of an encapsulated second material and allow it to work, such as a breaker. The technique further includes an operation to selectively release the chemical or the second chemical by performing the first release operation or the second release operation. The technique further includes an operation to attach the longitudinal body to a slickline, a wireline, a coiled tubing or a micro-coil tubing, and to deliver the longitudinal body to a specified depth with the tool. According to certain embodiments, the longitudinal body may be attached to the line with a connector able to release the longitudinal body. The connector may release the longitudinal body through an actuator which may respond to a chemical reaction, a mechanical trigger or physical trigger. The chemical reaction may be triggered by the treating fluid.

[0032] According to certain embodiments, the line may include adapters for weight bars to assist in its deployment to the desired depth in the wellbore.

[0033] Certain embodiments of the method include one or more of the operations described following. Operations described may be substituted, replaced, re-ordered,

divided, and/or grouped in various embodiments.

[0034] The foregoing disclosure and description of the invention is illustrative and explanatory thereof and it can be readily appreciated by those skilled in the art that various changes in the size, shape and materials, as well as in the details of the illustrated construction or combinations of the elements described herein can be made without departing from the spirit of the invention.

Claims

What is claimed is:

1. A method comprising:
 - (a) deploying through a well a substantially longitudinal body comprising at least in part a degradable material able to release a chemical;
 - (b) positioning the longitudinal body at a downhole location from the well; and
 - (c) allowing the degradable material to degrade and the chemical to be released.
2. The method of claim 1, wherein the longitudinal body is positioned on a tool selected from the group consisting of slickline, wireline, coil-tubing, micro-coil tubing, drill string, and combination thereof.
3. The method of claim 1, wherein the degradable material is degraded at the downhole location with addition of a release fluid, which is naturally present at downhole location or injected.
4. The method of claim 3, wherein the degradable material is degraded at the downhole location with a trigger.
5. The method of claim 5, wherein the trigger is selected from the group consisting of: temperature, mechanical wave including acoustic wave, and electromagnetic wave (microwave, UV).
6. The method of claim 1, wherein the longitudinal body further comprises at least in part a second degradable material able to release a second chemical.
7. The method of claim 6, wherein the chemical or the second chemical is selected from the group consisting of: polymer cross-linker, a breaker, an acid or an acid precursor, a polyacrylamide and mixtures thereof.
8. The method of claim 6, wherein the degradable material or the second degradable

material is selected from the group consisting of: lactide, glycolide, polylactic acid, polyglycolic acid, copolymers of polylactic acid and polyglycolic acid, copolymers of glycolic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties, copolymers of lactic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties, and mixtures thereof.

9. A method comprising:

- (a) deploying with a slickline through a well a substantially longitudinal cylindrical body attached to the slickline, wherein the longitudinal body comprises at least in part a degradable material able to release a chemical;
- (b) positioning with the slickline the longitudinal body at a downhole location from the well; and
- (c) allowing the degradable material to degrade and the chemical to be released.

10. The method of claim 9, wherein the degradable material is degraded at the downhole location with addition of a release fluid, which is naturally present at downhole location or injected.

11. The method of claim 9, wherein the degradable material is degraded at the downhole location with a trigger.

12. The method of claim 11, wherein the trigger is selected from the group consisting of: temperature, mechanical wave including acoustic wave, and electromagnetic wave (microwave, UV).

13. The method of claim 9, wherein the longitudinal body further comprises at least in part a second degradable material able to release a second chemical.

14. The method of claim 13, wherein the chemical or the second chemical is selected from the group consisting of: polymer cross-linker, a breaker, an acid or an acid

precursor, a polyacrylamide and mixtures thereof.

15. The method of claim 13, wherein the degradable material or the second degradable material is selected from the group consisting of: lactide, glycolide, polylactic acid, polyglycolic acid, copolymers of polylactic acid and polyglycolic acid, copolymers of glycolic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties, copolymers of lactic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties, and mixtures thereof.
16. A method comprising:
 - (a) adding to a tool selected from the group consisting of slickline, wireline, coil-tubing, micro-coil tubing, and drill string, a substantially longitudinal body comprising at least in part a degradable material;
 - (b) deploying the tool through a well;
 - (c) positioning with the tool the longitudinal body at a downhole location of the well; and
 - (d) allowing the degradable material to degrade and the chemical to be released.
17. The method of claim 16, wherein the chemical is selected from the group consisting of: polymer cross-linker, a breaker, an acid or an acid precursor, a polyacrylamide and mixtures thereof.
18. The method of claim 16, wherein the degradable material is selected from the group consisting of: lactide, glycolide, polylactic acid, polyglycolic acid, copolymers of polylactic acid and polyglycolic acid, copolymers of glycolic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties, copolymers of lactic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties, and mixtures thereof.

19. The method of claim 16, wherein the degradable material is degraded at the downhole location with addition of a release fluid, which is naturally present at downhole location or injected.
20. The method of claim 16, wherein the degradable material is degraded at the downhole location with a trigger.
21. The method of claim 20, wherein the trigger is selected from the group consisting of: temperature, mechanical wave including acoustic wave, and electromagnetic wave (microwave, UV).

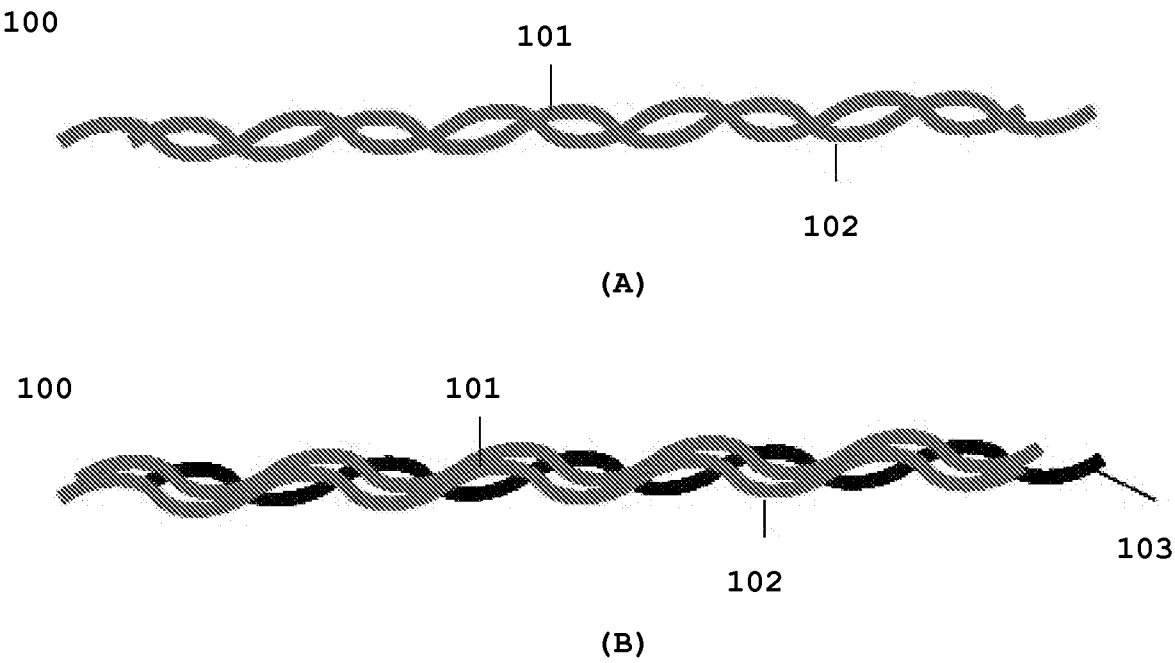


Figure 1