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(54) Title: USE OF REACTIVE SOLIDS AND FIBERS IN WELLBORE CLEAN-OUT AND STIMULATION APPLICATIONS

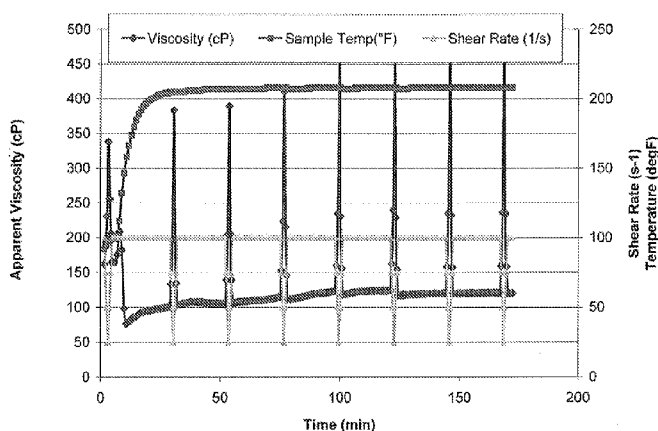


Figure 1

(57) Abstract: A method and apparatus to treat a subterranean formation including introducing a fluid comprising degradable material into a wellbore, contacting a surface of the wellbore with the fluid, and stimulating a surface of a subterranean formation, wherein the contacting the wellbore surface and stimulating the formation occur over a time period that is tailored by the properties of the degradable material. In some embodiments, the properties of the degradable material include a chemical composition, a surface area, a geometric shape of a particle of the material, a concentration of the material in the fluid, a density of the material, a dimension of a particle of the material, or a combination thereof.



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USE OF REACTIVE SOLIDS AND FIBERS IN WELLBORE CLEAN-OUT AND STIMULATION APPLICATIONS

BACKGROUND

FIELD

[0001] This invention relates to methods and fluids used in treating a subterranean formation. In particular, the invention relates to the preparation and use of reactive solids and fibers in wellbore clean-out and stimulation applications.

DESCRIPTION OF THE RELATED REFERENCES

[0002] This invention relates to a composition and method for stimulation and for removing impermeable layers created for fluid loss control in a subterranean formation. More particularly it relates to the use of a fluid containing a delayed solid acid material that can either remove drilling mud filtercakes or create a self-destructing filtercake in subterranean formations that require fluid loss control.

[0003] During drilling of a well, a thin layer of impermeable material is deposited on the reservoir rock by the drilling fluid (or mud). This thin layer of material is called a filtercake and aids in controlling drilling fluid leak-off into the formation and restricts the inflow of reservoir fluids into the well during completion. If the filtercake that is created during the drilling process is not removed prior to or during completion of the well, problems may occur when the well is put on production. These may include completion equipment failures, such as erosion and plugging of the equipment, and impaired reservoir productivity, which may be in the form of early water production or water coning.

[0004] The major components typically found in conventional drilling mud filtercake include such materials as polymers, carbonates and other inorganic salts, and clays. Removal of the mud filtercake can be accomplished through mechanical means (scrapping, jetting, underreaming, etc). Conventional chemical treatments for removing filtercake include pumping aqueous solutions with an oxidizer (such as persulfate), inorganic acids (such as HCl), organic acids (such as acetic or formic acids), chelating agents (such as EDTA), enzymes or combinations of these.

Generally, the oxidizer or enzyme digests the polymer layer in the filtercake and the acids dissolve the carbonate portion in the filtercake.

[0005] There are several problems that exist in conventional filtercake removal. The acids used tend to react very quickly with carbonate and “wormholes” are readily formed where most of the acid will funnel off through these small openings into the reservoir and leave most of the zone untreated. Oxidizers are very corrosive and reactive. They also must be pumped as a separate stage, which causes operational complexity and extra cost. Additionally, the lifetime of an oxidizer at higher temperatures may be only a few seconds. Enzyme breakers are extremely sensitive to pH, temperature, and ionic strength. They are not effective in breaking polymers in acidic solutions and will lose their activity at higher temperatures. Chelants are weak acids and poor dissolvers of carbonate compared to other organic acids, such as acetic and formic acid. Catalysts and activators require a second step in the completion process that causes additional operational costs.

[0006] There are many oilfield applications that require the use of fluid loss control agents in the near well-bore region, within the formation itself or against sand control screens and gravel packs. Some of these applications are in cased and perforated wellbores, while others are in open holes.

[0007] In some applications, enzyme or oxidizer soaks (to hydrolyze polymeric components of the filtercake) are performed, followed by an acid treatment. This process is also ineffective, since the reaction of the acid with carbonate bridging agents in the absence of coating with polymeric components (as it would be after the enzyme or oxidizer soak) is much faster than the reaction of acid with all components of the filtercake intact, causing the same problems.

[0008] Other alternatives include combining chelating agent solutions, which provides much slower reaction rates with much lower corrosion rates. Although enzyme and chelating agent solutions or chelating agent solutions alone have been effectively used in open hole completions, in longer wells, and particularly at higher temperatures, even they may react relatively quickly in long open hole completions. Thus, it is desirable to have a filtercake cleanup solution which is not reactive until after some time (e.g., until after the wash-pipe is pulled and the formation is

isolated). There is therefore a need to provide improvements in compositions and methods for filtercake removal and for providing effective and readily reversible fluid loss pills or treatments.

SUMMARY

[0009] Embodiments of this invention relate to a method to treat a subterranean formation including introducing a fluid comprising degradable material into a wellbore, contacting a surface of the wellbore with the fluid, and stimulating a surface of a subterranean formation, wherein the contacting the wellbore surface and stimulating the formation occur over a time period that is tailored by the properties of the degradable material. In some embodiments, the properties of the degradable material include a chemical composition, a surface area, a geometric shape of a particle of the material, a concentration of the material in the fluid, a density of the material, a dimension of a particle of the material, or a combination thereof. Some embodiments may benefit from the use of an oil-based system or a water-based system.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figure 1 shows the rheology of 5% NaCl brine and 6% erucic amidopropyl dimethyl betaine at 207 degrees F.

[0011] Figure 2 is a plot of pH as a function of time for Tests 1-3 of Table 2 at 158 degrees F.

[0012] Figure 3 is a plot of pH as a function of time for Tests 4-6 of Table 2 at 158 degrees F.

[0013] Figure 4 is a plot of pH as a function of time for Tests 7-9 of Table 3 at 158 degrees F.

[0014] Figure 5 is a plot of pH as a function of time for Tests 10-12 of Table 3 at 158 degrees F.

[0015] Figure 6 is a plot of pH as a function of time for Tests 1 and 3 of Table 2 at 200 degrees F.

[0016] Figure 7 is a plot of pH as a function of time for Tests 4 and 6 of Table 2 at 200 degrees F.

[0017] Figure 8 is a plot of pH as a function of time for Tests 7 and 9 of Table 3 at 200 degrees F.

[0018] Figure 9 is a plot of pH as a function of time for Tests 10 and 12 of Table 3 at 200 degrees F.

DESCRIPTION

[0019] At the outset, it should be noted that in the development of any such actual embodiment, numerous implementation—specific decisions must be made to achieve the developer's specific goals, such as compliance with system related and business related constraints, which will 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. In addition, the composition used/disclosed herein can also comprise some components other than those cited. 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 possessed knowledge of the entire range and all points within the range.

[0020] The statements made herein merely provide information related to the present disclosure and may not constitute prior art, and may describe some embodiments illustrating the invention.

[0021] There are many wellbore clean-out and stimulation systems currently in use in the upstream oil & gas industry. In general, the two processes are isolated from each other. The chemistry for both instances can vary substantially from one product to the other. Generally, the mud properties used in the productive section of a reservoir would dictate the chemistry of

wellbore cleanout system. One of the common components used as bridging agent in both water-based and oil-based mud systems is calcium carbonate particles with specific sizes and shapes. Various functional additives like mutual solvents and surfactants enable efficient contact with a reactive component in the system. This reactive component in the system can be an acid or chelant, and the component attacks the bridging agent to destabilize and dissolve the mud filtercake on the wellbore wall. The technical challenge resolved by embodiments of this invention is to make this reaction uniform and minimize losses during the process. Solid acid beads and fibers give a unique opportunity to delay or tailor reactions substantially and combine it with the stimulation step afterwards in carbonate formations.

[0022] The process of cleanout and stimulation happens simultaneously or one after the other. For example, once the solid acid hydrolyzes, acid is generated, then acid reacts with the filtercake, and any remaining hydrolyzed acid will react with the carbonate formation. In the wellbore, there is enough solid acid to react with carbonate material in the filter cake and additionally to react with the formation. The hydrolyzed acid performs a wellbore enlargement and/or fissure cleanout, which could be considered one stimulation technique. In some embodiments, hydrolysis of the solid or chelant, such as solid acid, will not be intermediate. Therefore, the non-hydrolyzed solid acid will form temporarily filtercake and will block any pinholes which would lead to more even mud cake dissolution; eventually all solid acid will hydrolyze and be consumed.

[0023] This technology utilizes solid acid, such as polylactic acid, to dissolve calcium carbonate-based filter cake from water based fluids. Also, the acid stimulates the near-wellbore region in openhole wells completed in carbonate formations. The solid acid is an inert substance under surface conditions but hydrolyzes into an acid under downhole conditions after a certain time influenced by bottomhole temperature. This mechanism will allow for a delayed reaction time which will be useful when it is placed with a rig after drilling the openhole section. It will give the rig time to pull out of hole and skid off the well before the acid reacts, preventing losses and well control issues. The solid acid will also simplify pumping operations since the fluid is non-corrosive and simple to place.

[0024] The solid acid will be mixed with a carrier fluid and pumped from the surface and placed in the openhole section. The solid acid will then hydrolyze and react with the near-wellbore

region, allowing for wellbore cleanout and matrix stimulation. This could be applied in hydrocarbon producing wells or water injection wells.

[0025] Degradable material like PLA, PGA, etc. could be used to enhance productivity or injectivity of wells as described here. Generally, as the material degrades, it releases acid that may stimulate the surfaces it encounters. Time and temperature of exposure will influence the solubility of the material and how the material degrades. Some embodiments may benefit from the use of a prepad treatment to cool the formation, which is especially important for high temperature wells when delay of the reaction is needed. The concentration of the material may be varied depending on various parameters of the system. Some embodiments may benefit from the material in concentrations of about 0.5 ppa of degradable material.

[0026] The pH of the fluid is important to how the system works. Specifically, the fluid should be tailored to have a neutral pH in a range of 5-8 pH. The pH will be reduced as the degradable solid hydrolyzes under downhole temperature and pressure. Also, having an initially neutral pH is critical to delaying filtercake dissolution. More reactive (higher or lower pH) systems may have premature breakthrough.

[0027] The density of the fluid may also be tailored to a specific optimized level. This optimized density may help maintain a specific hydrostatic level to deliver pressure downhole and to suspend degradable solid particles.

[0028] A. Spotting slurried degradable material after finishing drilling wellbore using circulation (direct or reverse) via drillstring, coiled tubing or jointed pipe or bullheading the slurried material into wellbore to create concentration of the degradable material. This material could not leak-off into formation and may act as fluid loss agent, although this is not the primary intention of the use. Degradation of the material is controlled by temperature of the subterranean formation so an appropriate material would be selected to provide sufficient time for retracting the pipe (if used for the placement) and run in the wellbore completion or otherwise prepare the well for production or injection. Degradation of the material via hydrolysis would result in forming a certain amount of organic acid. This acid would react with the bridging material of mud filtercake (typically calcium carbonate) and subterranean rock, thus enhancing its permeability to reservoir or injected fluids or gases. Low reaction rate of the acid also permits

squeezing it into formation either under pressure of hydrostatic column or intended injection. Degradable material could be in form of beads, fiber, chips, flakes, powder, or others. A combination of sized round particles could be used to enhance slurried degradable material ability to flow and reduce risk of leaving placement tubulars downhole if stuck due to local concentration of the material (degradable nature of material would make it possible to free pipe after a certain time, however, delay may not be desired). Use of degradable material as stand-alone stimulation system is desirable and differs from use of degradable solid beads in fracturing or fiber in matrix stimulation. Use of this material for mud filtercake removal also has a potential for long reaction retardation.

[0029] B. Adding degradable material to acid or non-acidic reactive solutions intended to dissolve mud filtercake to enhance its performance by forming temporarily barrier across zones of uneven dissolution (pinholes) to effectively prevent loss of fluid into subterranean formation and to keep it in the wellbore for uniform dissolution of the mentioned mud filtercake.

Degradable particles would later hydrolyze and in turn react with remaining bridging material of the filtercake or reactive material of formation similarly to above example. This is different from use of fiber-like degradable material for fluid diversion because diversion would occur after placement of the reactive solution.

[0030] C. Degradable material to be introduced into a stream of fluid injected into subterranean formations for pressure support or other reasons whenever increase of injectivity or alteration of its distribution along length of wellbore is desired. Once enough material is placed into the wellbore, injection could be temporarily suspended or slowed to allow temperature increase to promote hydrolysis of the degradable material into stimulation fluid which would react with the subterranean formation on wellbore face or by leaking into later, thus increasing its ability to receive more fluids or altering injectivity profile in a favorable manner. Slowing or suspending injectivity may not be required for certain degradable materials upon exposure to downhole temperatures. Such use of degradable particles as a sole stimulation system is desirable.

[0031] D. Continuous injection of degradable particles into fluid injected into subterranean formations for pressure support or other reasons whenever temporary alteration of injectivity profile is desired. Solids will divert flow away from fissures or thief zones allowing better sweep efficiency. Effect of the resulting cool-down could be used to prolong diversion. The suspension

of solids fed into the stream of injected fluid or temporarily suspension of the fluid injection would revert the injection profile.

[0032] Degradable materials, such as solid acids including solid polymeric acid, that may be used in this process include polylactic acid, polyglycolic acid, and benzoic acid. The solid polymeric acid precursor may be made from at least one of homopolymers of lactic acid, glycolic acid, hydroxybutyrate, hydroxyvalerate and epsilon caprolactone; random copolymers of at least two of lactic acid, glycolic acid, hydroxybutyrate, hydroxyvalerate, epsilon caprolactone, L-serine, L- threonine, and L-tyrosine; block copolymers of at least two of polyglycolic acid, polylactic acid, hydroxybutyrate, hydroxyvalerate, epsilon caprolactone, L-serine, L- threonine, and L-tyrosine; homopolymers of ethylenetherephthalate (PET), butylenetherephthalate (PBT) and ethylenenaphthalate (PEN); random copolymers of at least two of ethylenetherephthalate, butylenetherephthalate and ethylenenaphthalate; block copolymers of at least two of ethylenetherephthalate, butylenetherephthalate and ethylenenaphthalate; and combinations of these. The identity of the degradable material may be selected to optimize degradation delay based on the temperature of the formation. Polyglycolic acid may be more desirable when the formation temperature is low, polylactic may be more desirable when the formation temperature is above 150degF.

[0033] In one embodiment, the particulate material has a first average particle size and the degradable particulate material has a second average particle size, wherein the second average particle size is between three to twenty times smaller than the first average particle size. The second average particle size may be between five to ten times smaller than the first average particle size. In a second embodiment, the degradable particulate material has further an amount of particulates having a third average particle size, wherein the third average particle size is between three to twenty times smaller than the second average particle size. The third average particle size may be between five to ten times smaller than the second average particle size.

[0034] The particulate material may be of any geometry that is appropriate for the task. Fibers, flakes, cylinders, round, oblong, rod-like, beads, or other shapes that are selected for their dimensions, high-aspect-ratio size, surface area to volume ratio, surface area, volume, or any other geometry parameter that may be tailored to help the material degrade with a desired profile.

Some embodiments may benefit from a mixture of particle shapes or sizes. Some embodiments may benefit from a mixture of degradable and non-degradable materials.

[0035] The carrier fluid for the solid acid may be any variety of fluids including drilling muds, drilling fluids, fracturing fluids, and other fluids employed by the oil field services industry. Water-based fluids may benefit from the optional inclusion of additional additives including enzymes, surfactant, microemulsion, demulsifier, acid, buffers, (mutual) solvent, and corrosion inhibitor. Oil-based fluids may also benefit from the optional inclusion of additional additives including surfactants, microemulsions, solvents, demulsifier, and corrosion inhibitor. The concentration of additives in oil-based muds may be higher than the concentration in water-based muds. Further, the oil-based fluid systems may benefit from a solvent based preflush step.

[0036] Generally, oil based mud may contain oil (linear paraffin, diesel, etc., water, calcium chloride, primary and secondary emulsifiers, viscosifiers such as modified clay, lime, fluid loss agent, and weighing agent such as barite or calcium carbonate. Some oil-based fluids may be an invert emulsion, *i.e.*, emulsions in which the non-oleaginous fluid is the discontinuous phase and the oleaginous fluid is the continuous phase.

[0037] The oleaginous fluid may be a liquid and more preferably is a natural or synthetic oil and more preferably the oleaginous fluid is selected from the group including diesel oil; mineral oil; a synthetic oil, such as hydrogenated and unhydrogenated olefins including polyalpha olefins, linear and branch olefins and the like, polydiorganosiloxanes, siloxanes, or organosiloxanes, esters of fatty acids, specifically straight chain, branched and cyclical alkyl ethers of fatty acids, mixtures thereof and similar compounds known to one of skill in the art; and mixtures thereof. The concentration of the oleaginous fluid should be sufficient so that an invert emulsion forms, and the concentration of the oleaginous fluid may be less than about 99% by volume of the invert emulsion. In one embodiment the amount of oleaginous fluid is from about 30% to about 95% by volume of the invert emulsion fluid and more preferably about 40% to about 90% by volume of the invert emulsion fluid. The oleaginous fluid in one embodiment may include at least 5% by volume of a material selected from the group including esters, ethers, acetals, dialkylcarbonates, hydrocarbons, and combinations thereof.

[0038] The non-oleaginous fluid used in the formulation of the invert emulsion fluid disclosed herein may be a liquid and preferably may be an aqueous liquid. More preferably, the non-oleaginous liquid may be selected from the group including sea water, a brine containing organic and/or inorganic dissolved salts, liquids containing water-miscible organic compounds and combinations thereof. The amount of the non-oleaginous fluid is typically less than the theoretical limit needed for forming an invert emulsion. Thus in one embodiment the amount of non-oleaginous fluid is less than about 70% by volume of the invert emulsion fluid and preferably from about 1% to about 70% by volume of the invert emulsion fluid. In another embodiment, the non-oleaginous fluid is preferably from about 5% to about 60% by volume of the invert emulsion fluid.

[0039] Also typically included are emulsifiers and emulsifier systems for stabilizing the emulsion. As used herein, emulsifier, emulsifying agent, and surfactant are used interchangeably. The emulsifying agent serves to lower the interfacial tension of the liquids so that the non-oleaginous liquid may form a stable dispersion of fine droplets in the oleaginous liquid. A full description of such invert emulsions may be found in *Composition and Properties of Drilling and Completion Fluids*, 5th Edition, H. C. H. Darley, George R. Gray, Gulf Publishing Company, 1988, pp. 328-332.

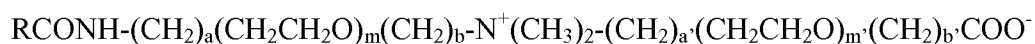
[0040] Emulsifiers that may be used in the fluids disclosed herein include, for example, fatty acids, soaps of fatty acids, amidoamines, polyamides, polyamines, oleate esters, such as sorbitan monooleate, sorbitan dioleate, imidazoline derivatives or alcohol derivatives and combinations or derivatives of the above. Additionally, the fluid may also contain surfactants that may be characterized as wetting agents. Wetting agents that may be suitable for use in the fluids disclosed herein include crude tall oil, oxidized crude tall oil, organic phosphate esters, modified imidazolines and amidoamines, alkyl aromatic sulfates and sulfonates, and the like, and combinations or derivatives of these. However, when used with the invert emulsion fluid, the use of fatty acid wetting agents should be minimized so as to not adversely affect the reversibility of the invert emulsion disclosed herein. FAZE-WET[®], VERSACOAT[®], SUREWET[®], VERSAWET[®], and VERSAWET[®] NS are examples of commercially available wetting agents manufactured and distributed by M-I L.L.C. of Houston, Texas that may be used in the fluids disclosed herein.

[0041] In a particular embodiment, the invert emulsion may be of the reversible type, whereby the invert emulsion may be converted from a water-in-oil type emulsion to an oil-in-water type emulsion upon exposure to acid, for example. Such reversible oil-based fluids include those described in U.S. Patent Nos. 6,218,342, 6,806,233 6,790,811, 7,527,097, 7,238,646, 6,989,354, 7,178,550, 6,608,006, 7,152,697, 7,178,594, 7,222,672, 7,238,646 and 7,377,721.

[0042] The viscosity of the fluid may be tailored to maintain suspension of degradable solid particles uniformly along the length of openhole sections to minimize settling. To control the fluid viscosity, a variety of additives may be used including viscoelastic surfactants and polymers such as guar, HEC, xanthan, guar derivative, cellulose, cellulose derivative, heteropolysaccharide, heteropolysaccharide derivative, polyacrylamide, CMHPG, cationic guar, diutan, partially hydrolyzed polyacrylamide, copolymers of partially hydrolyzed polyacrylamide alginate, chitosan, or a combination thereof.

[0043] In embodiments of the invention, systems of the invention made of degradable solid acids are especially useful in conjunction with viscoelastic surfactant (VES) fluid system. VES fluid system is a fluid viscosified with a viscoelastic surfactant and any additional materials, such as but not limited to salts, co-surfactants, rheology enhancers, stabilizers and shear recovery enhancers that improve or modify the performance of the viscoelastic surfactant.

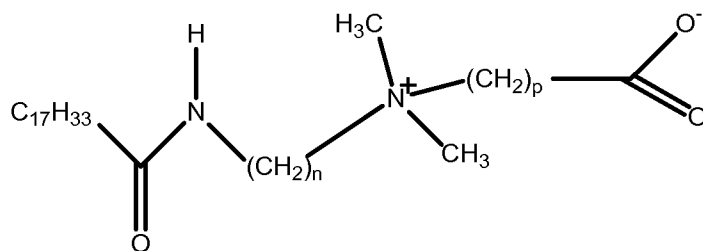
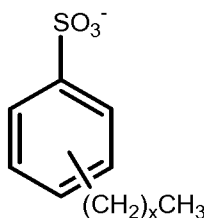
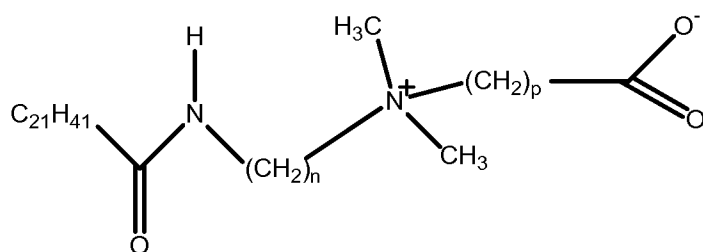
[0044] The useful VES's include cationic, anionic, nonionic, mixed, zwitterionic and amphoteric surfactants, especially betaine zwitterionic viscoelastic surfactant fluid systems or amidoamine oxide viscoelastic surfactant fluid systems. Examples of suitable VES systems include those described in U.S. Pat. Nos. 5,551,516; 5,964,295; 5,979,555; 5,979,557; 6,140,277; 6,258,859 and 6,509,301. The system of the invention is also useful when used with several types of zwitterionic surfactants. In general, suitable zwitterionic surfactants have the formula:



[0045] in which R is an alkyl group that contains from about 14 to about 23 carbon atoms which may be branched or straight chained and which may be saturated or unsaturated; a, b, a', and b' are each from 0 to 10 and m and m' are each from 0 to 13; a and b are each 1 or 2 if m is not 0 and (a+b) is from 2 to about 10 if m is 0; a' and b' are each 1 or 2 when m' is not 0 and (a'+b') is from 1 to about 5 if m is 0; (m+m') is from 0 to about 14; and the O in either or both CH₂CH₂O

groups or chains, if present, may be located on the end towards or away from the quaternary nitrogen.

[0046] Preferred zwitterionic surfactants include betaines. Two suitable examples of betaines are BET-O and BET-E. The surfactant in BET-O-30 is shown below; one chemical name is oleylamidopropyl betaine. It is designated BET-O-30 because as obtained from the supplier (Rhodia, Inc. Cranbury, New Jersey, U. S. A.) it is called Mirataine BET-O-30 because it contains an oleyl acid amide group (including a $C_{17}H_{33}$ alkene tail group) and contains about 30% active surfactant; the remainder is substantially water, sodium chloride, and propylene glycol. An analogous material, BET-E-40, is also available from Rhodia and contains an erucic acid amide group (including a $C_{21}H_{41}$ alkene tail group) and is approximately 40% active ingredient, with the remainder being substantially water, sodium chloride, and isopropanol. VES systems, in particular BET-E-40, optionally contain about 1 % of a condensation product of a naphthalene sulfonic acid, for example sodium polynaphthalene sulfonate, as a rheology modifier, as described in U. S. Patent No. 7,084,095. The surfactant in BET-E-40 is also shown below; one chemical name is erucylamidopropyl betaine. BET surfactants, and other VES's are described in U. S. Patent No. 6,258,859. BET surfactants make viscoelastic gels when in the presence of certain organic acids, organic acid salts, or inorganic salts; in that patent, the inorganic salts were present at a weight concentration up to about 30%. Co-surfactants may be useful in extending the brine tolerance, and to increase the gel strength and to reduce the shear sensitivity of the VES-fluid, in particular for BET-O-type surfactants. An example given in U. S. Patent No. 6,258,859 is sodium dodecylbenzene sulfonate (SDBS), also shown below. Other suitable co-surfactants include, for example those having the SDBS-like structure in which $x = 5 - 15$; preferred co-surfactants are those in which $x = 7 - 15$. Still other suitable co-surfactants for BET-O-30 are certain chelating agents such as trisodium hydroxyethylethylenediamine triacetate. The rheology enhancers may be used with viscoelastic surfactant fluid systems that contain such additives as co-surfactants, organic acids, organic acid salts, and/or inorganic salts.

Surfactant in BET-O-30 (when $n = 3$ and $p = 1$)Surfactant in BET-E-40 (when $n = 3$ and $p = 1$)

SDBS (when $x = 11$ and the counterion is Na^+)

[0047] Some embodiments use betaines; for example BET-E-40. Although experiments have not been performed, it is believed that mixtures of betaines, especially BET-E-40, with other surfactants are also suitable.

[0048] Other betaines that are suitable include those in which the alkene side chain (tail group) contains 11 – 23 carbon atoms (not counting the carbonyl carbon atom) which may be branched or straight chained and which may be saturated or unsaturated, $n = 2 - 10$, and $p = 1 - 5$, and mixtures of these compounds. Betaines are those in which the alkene side chain contains 11 – 21 carbon atoms (not counting the carbonyl carbon atom) which may be branched or straight chained and which may be saturated or unsaturated, $n = 3 - 5$, and $p = 1 - 3$, and mixtures of

these compounds. These surfactants are used at a concentration of about 0.5 to about 10%, or from about 1 to about 6%, and or from about 1.5 to about 6%. In some embodiments, erucic amidopropyl dimethyl betaine may be selected, which is commercially available from Rhodia of Cranbury, New Jersey.

[0049] Although the invention has been described using the term “VES”, or “viscoelastic surfactant” to describe the non-polymeric viscosified well treatment fluids, other non-polymeric materials may also be used to viscosify the fluid provided that the requirements described herein for such a fluid are met, for example the required viscosity, stability, compatibility, and lack of damage to the wellbore, formation or fracture face.

EXAMPLES

[0050] The following examples are presented to illustrate the preparation and properties of fluid systems, and should not be construed to limit the scope of the invention, unless otherwise expressly indicated in the appended claims. All percentages, concentrations, ratios, parts, etc. are by weight unless otherwise noted or apparent from the context of their use.

[0051] Testing was performed to examine a wellbore cleanout fluid utilizing solid polylactic acid intended for water-based mud (WBM) applications. The base cleanout fluid was 5% NaCl brine; in order to obtain good suspension of solid polylactic acid, 6% was utilized as viscosifier. Rheology of the viscous carrier 5% NaCl brine + 6% erucic amidopropyl dimethyl betaine was also tested at 207 degF. The testing shows that the optimized fluid maintains viscosity above 100cP at 100sec-1 for more than 3 hours.

[0052] WBM mud cake dispersion and dissolution tests were conducted on mud cakes prepared on both filter paper and on a core plug; the dissolution fluid in this testing included 1PPA solid polylactic acid in the carrier fluid 5% NaCl brine + 6% erucic amidopropyl dimethyl betaine.

The conclusions are listed below:

- Testing on filter paper shows 2.2%, 7.6%, 54% and 100% dispersion/dissolution of the filtercake after 4, 8, 24 and 48 hours, respectively, at 207degF.
- Roughly 32% of solid polylactic acid solids remained unhydrolysed after the testing.
- Dissolution of a mud cake prepared on a core plug at 207degF and 300psi differential pressure shows 68% dispersion and dissolution after 3 days soaking

- In the core plug experiment, again 35% of solid polylactic acid remaining unhydrolyzed after the testing.
- It is recommended from these preliminary results to reduce the overall concentration of solid polylactic acid below 1PPA in field execution.

Rheology 5% NaCl Brine + 6% erucic amidopropyl dimethyl betaine

- Measure the required amount of water and pour into a Waring blender.
- Add in the required amount of NaCl
- Add in the required amount of erucic amidopropyl dimethyl betaine into the brine
- Shear the fluid at high RPM ~ 12000rpm
- Remove the air bubbles by centrifuging the fluid
- Once the air bubbles are remove, measure 50 mL of the fluid and pour it into HPHT rheometer cup. Apply 400 psi and run shear ramps as per API RP 39 starting at room temperature up to 207 degF [97 degC]
 - A B5 bob is used for the test and shear ramping: 118 rpm (100 s^{-1}), 88.5 rpm (75 s^{-1}), 59 rpm (50 s^{-1}), 29.5 rpm (25 s^{-1}), 59 rpm (50 s^{-1}), 88.5 rpm (75 s^{-1}), 118 rpm (100 s^{-1}).
 - Interval stir rate is set at 118 rpm (100 s^{-1}) between each temperature interval.

** M5600 HPHT rheometers manufactured by Grace Instruments were used. Test shear rates and viscosity calculations follow API Recommended Procedure 39.

Water Based Mud Cake Dispersion and Dissolution

- Water-based mud cake (with CaCO_3 bridging particles) was prepared on a filter paper.
- The mud cake was divided into four parts (each for 4, 8, 24, 48 and 72 hours testing)

- The initial weight of each mudcake was recorded.
- The wellbore cleanout fluid as per method 2.1 above with 1PPA solid polylactic acid was performed.
- The mudcake was placed into a beaker
- 200mL of wellbore cleanout fluid was poured into the beaker with mudcake.
- The beaker was placed into water bath at 200degF.
- The pH of the solution by time was checked.
- After 24, 48 and 72 hours take out the respective beaker, the final weight of the mud cake was measured.

Water Based Mud Cake Dispersion and Dissolution on Core Plug

- Saturate the core plug with 5% NaCl brine
- Measure the weight of the core plug setup without mudcake
- CaCO₃ based mud cake is prepared on a Berea Core Plug (150mD) by applying 500psi differential pressure.
- After 6 hours, remove and take pictures of the mud cake obtained
- Measure the initial weight of the core plug setup with mudcake
- Mix the wellbore cleanup fluid as per method 2.1 above with 1PPA solid polylactic acid
- Pour 100mL of wellbore cleanout fluid into the cell with mudcake.
- Place the cell into heater jacket at 200degF
- Apply 500psi pressure at the top of the cell and 200psi back-pressure at the bottom of the cell
- Let the treatment fluid soak for 3 days
- Collect the filtrate from the bottom of the cell versus time and check the pH and measure [Ca] concentration using ICP
- Weigh the core with residual mud cake to calculate mass of final mud cake.

[0053] Rheology of 5% NaCl brine + 6% erucic amidopropyl dimethyl betaine

[0054] Figure 1 illustrates the rheology of 5% NaCl brine and 6% erucic amidopropyl dimethyl betaine at 207degF. It provides a baseline viscosity and shear rate that are relatively stable over 120 minutes.

Mud Cake Dispersion and Dissolution

[0055] Visual inspection, as recorded by photographs, compared initial mud cake to the mud cake over time on filter paper. After 4 hours, 2.2% of the mud cake was dissolved and dispersed and after 8 hours, 7.6% dissolved and dispersed. After 24 hours 54% dissolved and dispersed and after 48 and 72 hours, the mud cake was completely dissolved and dispersed.

[0056] Visual inspection tests, as recorded by photographs, also compared solids in a beaker over time. The test showed unhydrolyzed polylactic acid remained as a solid in the beaker after 72 hours. Approximately 32% solid remained.

Mud Cake Dispersion and Dissolution in Core Plug

[0057] Core plug tests were also visually inspected and recorded by photographs. The tests of the core plug after 3 days soaking at 207degF showed that roughly 68% (w/w) of the mud cake is dispersed/dissolved. About 35% of the polylactic acid solids remain un-dissolved.

[0058] Next, the volume, pH and calcium content of the filtrate collected over time were recorded and are summarized below in Table 1.

Table 1 – Filtrate Analysis

Time (hours)	Accumulative Volume of Filtrate Collected (mL)	pH (pH paper)	Calcium Content (mg/L)
6	3	8	272.5
8	4	7	1843.6
24	10	4	25651.2
48	20 (flowing continuously)	3	> 40000

*Note: At 48 hours filtrate is flowing continuously, with total volume collected 10mL. The remaining fluid is left in the cell to soak for 3 days.

[0059] As described above, WBM mud cake dispersion and dissolution tests were conducted on mud cakes prepared on both filter paper and on a core plug; the dissolution fluid in this testing included 1PPA solid polylactic acid in the carrier fluid 5% NaCl brine + 6% erucic amidopropyl dimethyl betaine. From these tests, one can conclude the following.

- Testing on filter paper shows 2.2%, 7.6%, 54% and 100% dispersion/dissolution of the filtercake after 4, 8, 24 and 48 hours, respectively, at 207degF.
- Roughly 32% of polylactic acid solids remained unhydrolysed after the testing.
- Dissolution of a mud cake prepared on a core plug at 207degF and 300psi differential pressure shows 68% dispersion and dissolution after 3 days soaking.
- In the core plug experiment, again 35% of solid polylactic acid remaining unhydrolyzed after the testing.
- In field execution, it is recommended to reduce the overall concentration of solid polylactic acid below 1PPA.

[0060] Testing was performed to examine a wellbore cleanout fluid utilizing solid polylactic acid intended for oil based mud (OBM) applications in general. The treatment fluid consists of based fluid which is 11ppg NaBr brine, 50gallon/1000gallon of proprietary amine oxide surfactant, 25gallon/1000gallon of ethyleneglycol monobutyl ether (EGMBE), 2 gallon/1000gallon of acid corrosion inhibitor and 0.5PPA of PLA-2040.

[0061] The efficiency of the oil based mud (OBM) filter cake removal tests were conducted on mud cake formed by both filter paper (2.5 in specially hardened filter paper) and ceramic filter disc (0.4darcy/3 micron). The conclusions of the tests follows.

[0062] Testing on filter paper indicated that 100% dispersion/dissolution of the filtercake after 3days (72hours) at 207 degF.

[0063] 100% of the solid polylactic acid hydrolyzed after 12 days at 207degF. No solid acid was observed but only some oil residue remained.

[0064] The test was conducted with the same treatment fluid at different temperature. 100% of solid polylactic acid was hydrolyzed after 3 days at 250degF. No significant hydrolyzed of solid

polylactic acid after 13 days at 150degF. The solid polylactic acid hydrolyzed faster at higher temperature.

[0065] The retain permeability test was conducted by utilized the ceramic filter disc, 100% hydrolyzed of solid polylactic acid was observed after 12days of soaking at 207 degF. The retained permeability of the ceramic filter disc was 89.57%.

Oil Based Mud Cake Dispersion and Dissolution on filter paper

- Weigh the empty filter paper. (w1)
- Using the High temperature and high pressure fluid loss cell and heating jacket, create mud-cake on the filter paper by applying 300psi differential pressure at 207 degF. Stop the mud cake formation after collect the filtrate approximates 4-6ml.
- Remove the mud-cake from the cell.
- Mud-cake was divided into 4 equal parts, take each part for the different tests.
- Weigh the mud-cake with the filter paper as w2.
- Immersed the mud-cake and filter paper into 250ml of bottle with 200ml of testing fluid solution.
- The test bottle was placed into the pre-heated oven at 207degF for 12 days.
- Check the physical appearance of the mud-cake in the test bottle from time to time.
- Remove the remained mud-cake with filter paper after 12 days of soaking and weigh the mud-cake remained on filter paper as w3.
- Calculate the solubility and dispersing with the following formulation.

$$\text{Solubility and dispersing percentage} = \frac{(w2-w3)}{(w2-w1)} \times 100$$

Retained permeability determination by ceramic disc

- Vacuum to saturate the ceramic disc in 3%KCl brine.
- Weigh the initial weight of the saturated ceramic disc.
- The disc was loaded into the 500ml HPHT fluid loss cell. Determine the initial permeability in the production direction using 3% KCl by recording the differential pressure at various flowrates.

- Pour the oil based mud into the HTHP fluid loss cell and apply 300psi differential pressure to make the mud-cake. Heat up the cell to 207degF. Cool down the cell after obtained the filtrate approximates 4-6ml.
- Pour in the treatment fluid into the HTHP cell. Heat the cell up to 207degF and apply 300psi differential pressure. Soak the treatment fluid at the designated testing pressure and temperature for 12 days.
- Bled off the pressure and removed the treatment fluid from the cell.
- Fill the cell with 3%KCl to measure the final permeability. The final permeability is measure by injecting the brine in production direction with differential pressure at various rates. The retained permeability is calculate by

$$\text{Retained permeability} = \frac{\text{Final Permeability}}{\text{Initial Permeability}} \times 100$$

Oil Based Mud Cake Dispersion and Dissolution (on filter paper)

[0066] Visual inspection on physical appearance of the initial mud cake to the mud cake change over time on filter paper. The mud cake and filter paper was soaked in the treatment fluid consists of based fluid which is 11ppg NaBr brine, 50gallon/1000gallon of proprietary amine oxide surfactant, 25gallon/1000gallon of ethyleneglycol monobutyl ether (EGMBE), 2 gallon/1000gallon of acid corrosion inhibitor and 0.5PPA of PLA-2040. After 4 days of soaking, only 47.90% of mud cake dissolved and dispersed. 98% of mud cake dissolved and dispersed after 12 days of soaking at 207 degF. Solid polylactic acid dissolved 100% after 12 days of soaking at 207 degF.

[0067] The same treatment fluid were tested at difference temperature; 150degF, 207degF and 250degF. Solid polylactic acid dissolved 100% after 12 days soaking at 207degF and after 3 days soaking at 250degF. Significant of un-dissolved solid polylactic acid was observed after 13 days soaking at 150degF. On the other hand, more than 97% of the mud cake dissolved after 12 days soaking at 207degF and 3 days soaking at 250degF.

[0068] Solid polylactic acid was replaced with acetic acid in the treatment fluid to measure the difference in reactivity between the solid polylactic acid and the acetic acid. 47.9% of mud cake dissolved and dispersed after 4 days of soaking at 207degF with the treatment fluid contains

solid polylactic acid. 86% of the mud cake dissolved and dispersed after 2 days of soaking at 207degF with the treatment fluid contains acetic acid. This indicate the solid polylactic acid have some delay in reaction.

Retained permeability for the oil based mud

[0069] The initial permeability of the clean ceramic disc was determined, oil based mud cake was formed with the ceramic disc. The treatment fluid consists of based fluid which is 11ppg NaBr brine, 50gallon/1000gallon of proprietary amine oxide surfactant, 25gallon/1000gallon of ethyleneglycol monobutyl ether (EGMBE), 2 gallon/1000gallon of acid corrosion inhibitor and 0.5PPA of PLA-2040 was poured into the HTHP cell and soaked for 12 days at 207 degF. Final permeability of the ceramic disc was obtained. The 89.57% of retained permeability show good oil based mud-cake removal property.

[0070] The next set of experiments compares solid acid size, calcium carbonate presence, temperature, and brine medium for the treatment fluid apply to oil based mud (OBM)

Tables 2 and 3 – Brine, acid mesh size, and calcium carbonate mass.

	Test1	Test 2	Test 3	Test4	Test 5	Test 6
Brine used	2%KCl	2%KCl	2%KCl	2%KCl	2%KCl	2%KCl
vol of brine,ml	42	42	42	42	42	42
wt of PLA-2040,g	2.5158	2.5	2.5			
wt of PLA-100,g				2.5	2.5	2.5
wt of CaCO3		25.2	12.6		25.2	12.6

	Test7	Test 8	Test 9	Test10	Test 11	Test 12
Brine used	12.5ppgNaBr	12.5ppgNaBr	12.5ppgNaBr	12.5ppgNaBr	12.5ppgNaBr	12.5ppgNaBr
vol of brine,ml	42	42	42	42	42	42
wt of PLA-2040,g	2.5	2.5	2.5			
wt of PLA-100,g				2.5	2.5	2.5
wt of CaCO3		25.2	12.6		25.2	12.6

[0071] The results of these tests are illustrated by Figures 5 to 9. Specifically, 100 mesh PLA is more reactive than 2040 mesh PLA. Also, calcium carbonate does not accelerate the hydrolysis process, it neutralizes the fluid pH. Higher temperature accelerates the hydrolysis process. A concentration of 60 or 30 weight percent calcium carbonate did not yield significantly different results. The brine identity (NaBr or KCl) did not yield significantly different results.

Table 4 – Summary of results from tests described by Tables 2 and 3

	Test 1	Test 2	Test 3	Test 4	Test 5
Brine used	11.34 ppg NaBr	11.34 ppg NaBr	11.34 ppg NaBr	11.34 ppg NaBr	Distilled water
PLA-2040	0.1ppa	0.2 ppa	0.3 ppa	0.4 ppa	0.1 ppa
Curing Period	6 days	6 days	6 days	6 days	6 days
Curing Temperature	203 degF	203 degF	203 degF	203 degF	203 degF
Final Fluid pH	1.19	1.18	1.23	0.56	2.13
% of solid acid soluble	53.00	47.00	47.00	47.00	45.00

[0010] This shows that the solubility of the solid acid is approximate 50% for 6 days curing regardless of the initial concentration. This table also generally shows that the solubility of the solid acid is dependent to time and not depend on the concentration. Some testing indicated that it may take more than 11 days to hydrolyze all PLA for some of the material tested. Additional testing that was visually observed and photographed showed that 4 days was insufficient to hydrolyze all PLA, but that after 12 days, no solid acid was residual and some oil residue remained.

[0011] The particular embodiments disclosed above are illustrative only, as the invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details herein shown, other than as described in the claims below. It is therefore evident that the particular embodiments disclosed above may be altered or modified and all such variations are considered within the scope and spirit of the invention. Accordingly, the protection sought herein is as set forth in the claims below.

CLAIMS

What is claimed is:

1. A method for treating a subterranean formation, comprising:
introducing a fluid comprising degradable material into a wellbore;
contacting a surface of the wellbore with the fluid; and
stimulating a surface of a subterranean formation,
wherein the contacting the wellbore surface and stimulating the formation occur over a time period that is tailored by the properties of the degradable material.
2. The method of claim 1, wherein the properties of the degradable material comprise a chemical composition, a surface area, a geometric shape of a particle of the material, a concentration of the material in the fluid, a density of the material, a dimension of a particle of the material, or a combination thereof.
3. The method of claim 1, wherein the time period is 48 hours or more.
4. The method of claim 1, wherein the fluid further comprises surfactant.
5. The method of claim 4, wherein the surfactant comprises viscoelastic surfactant.
6. The method of claim 5, wherein the viscoelastic surfactant comprises betaine.
7. The method of claim 1, wherein the fluid comprises corrosion inhibitor.
8. The method of claim 1, wherein the fluid comprises mutual solvent.
9. The method of claim 1, wherein the degradable material is a chelating agent.
10. The method of claim 1, wherein the degradable material has an amount of particulates with average particle size and a second amount of particulates with a second average particle size, wherein the second average particle size is between three to twenty times smaller than the first average particle size.
11. The method of claim 10, wherein the second average particle size is between five to ten times smaller than the first average particle size.
12. The method of claim 11, wherein the degradable material has a further amount of particulates having a third average particle size, wherein the third average particle size is between three to twenty times smaller than the second average particle size.

13. The method of claim 12, wherein the third average particle size is between five to ten times smaller than the second average particle size.
14. The method of claim 1, wherein the fluid further comprises calcium carbonate particles.
15. The method of claim 1, wherein the fluid comprises corrosion inhibitor, mutual solvent, surfactant.

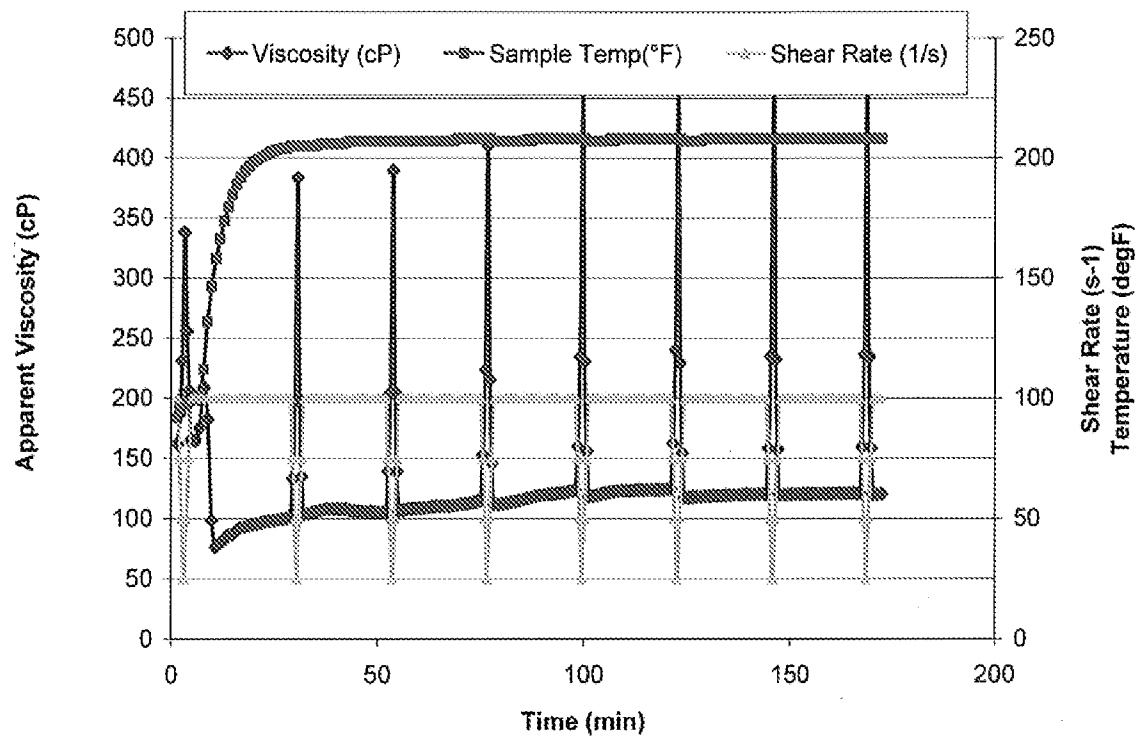


Figure 1

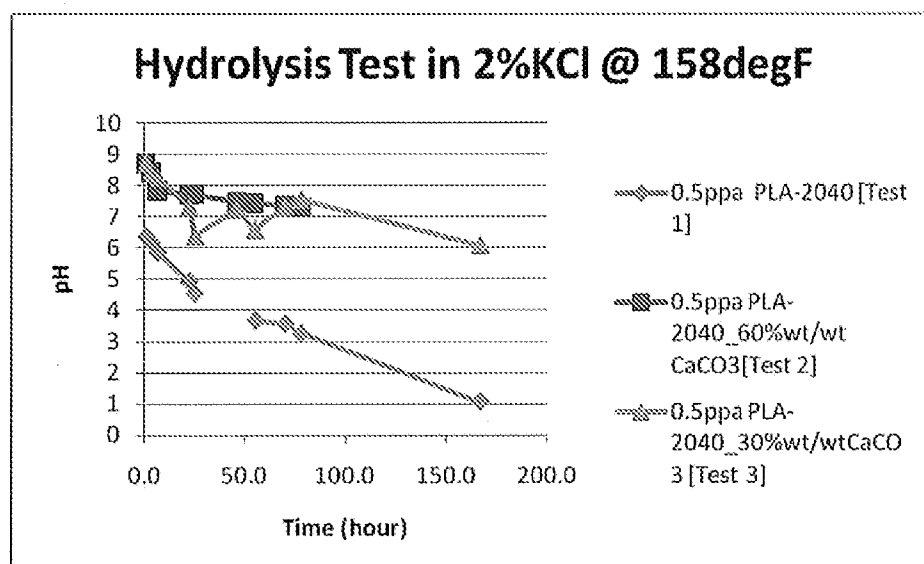


Figure 2

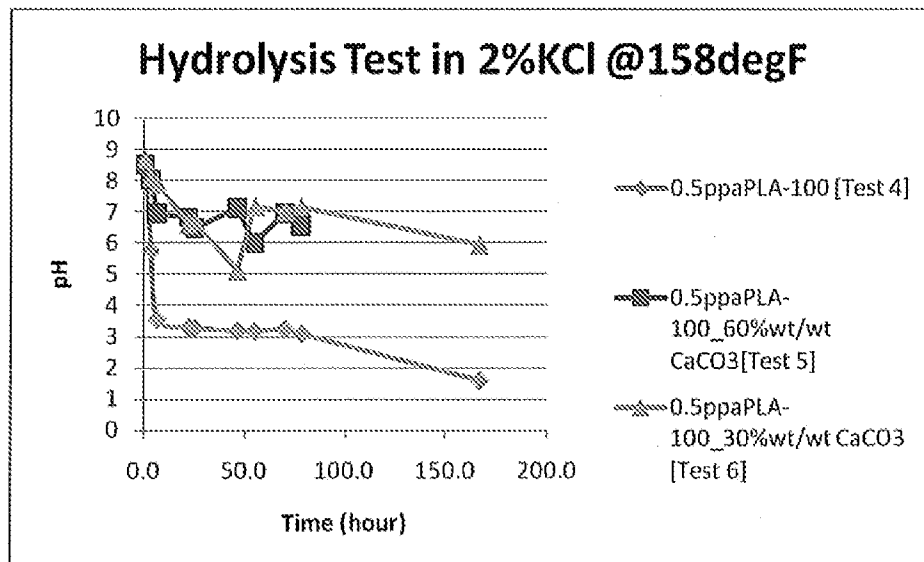


Figure 3

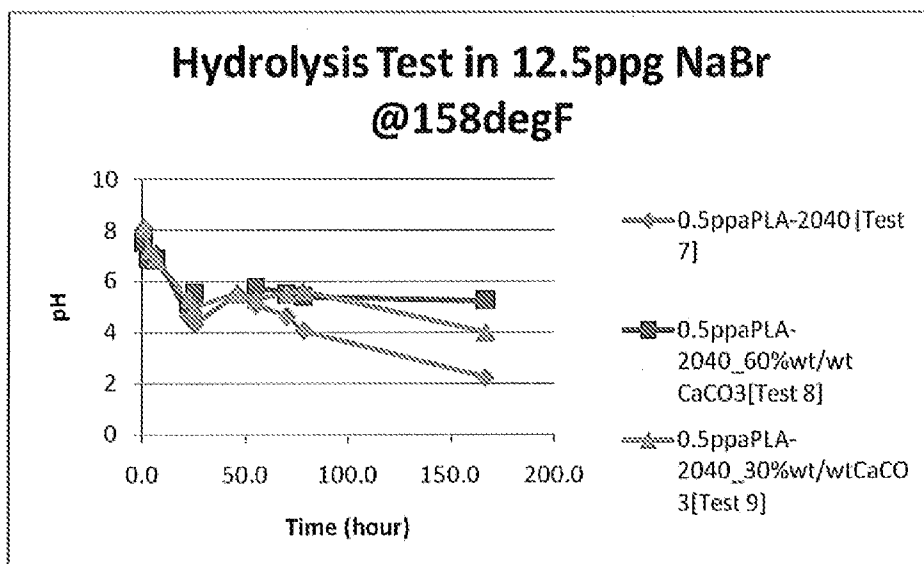


Figure 4

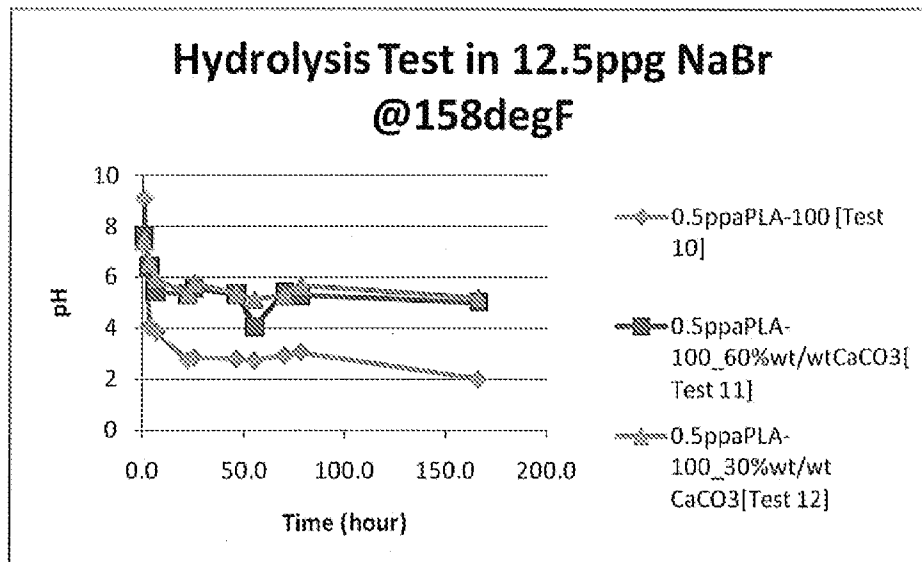


Figure 5

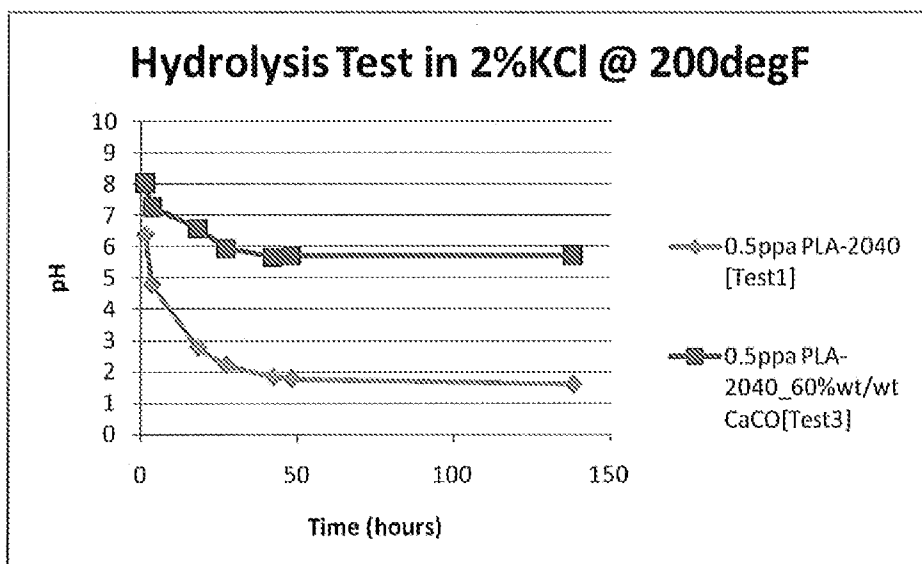


Figure 6

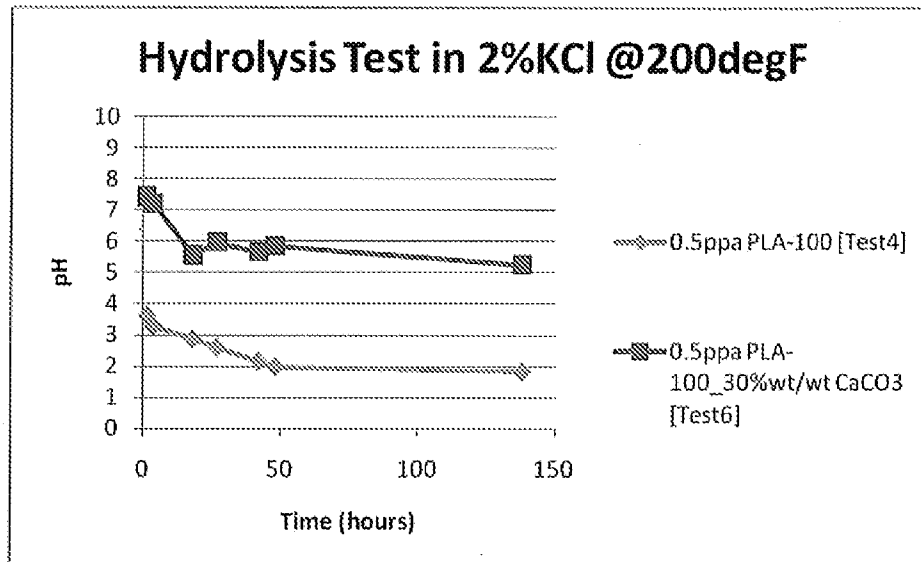


Figure 7

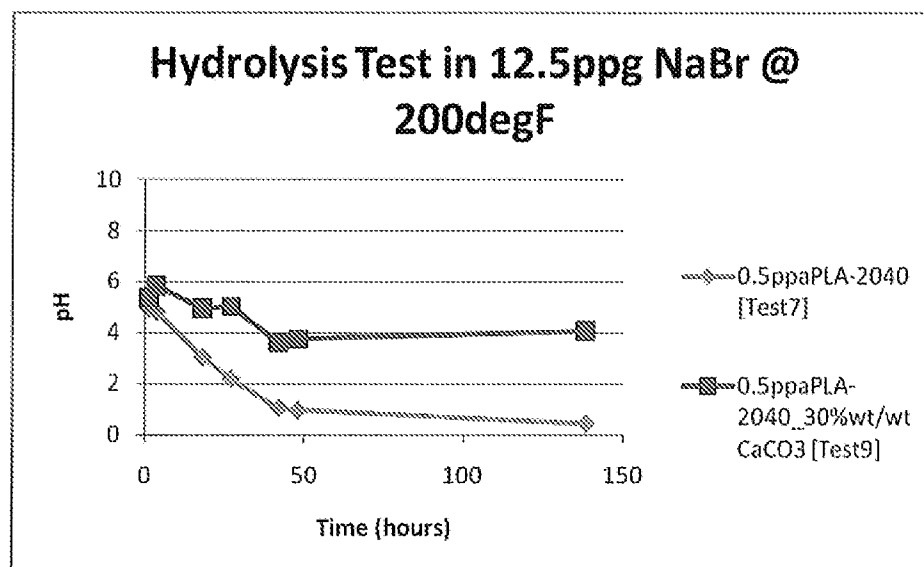


Figure 8

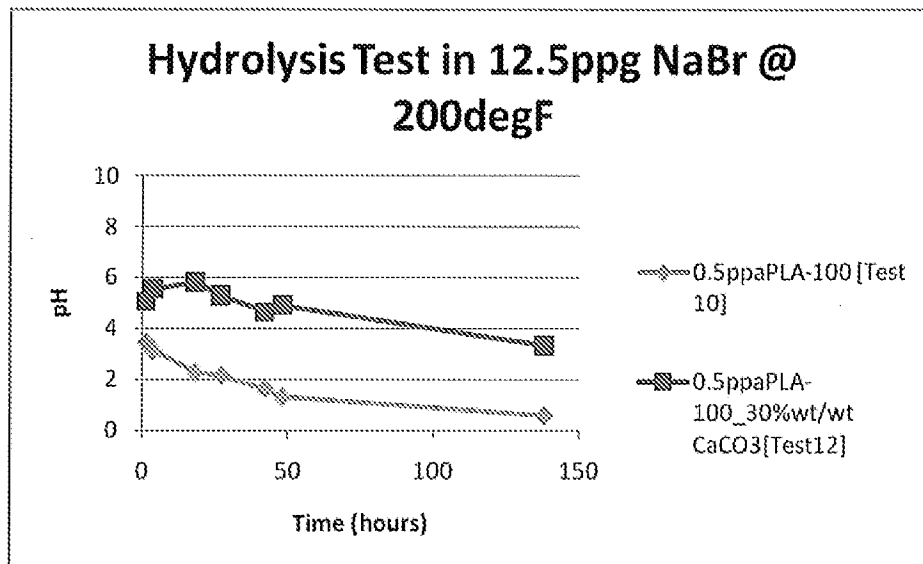


Figure 9