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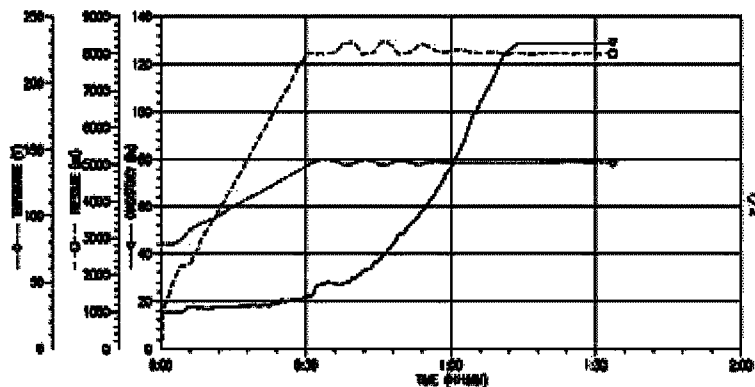
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(54) Title **Liquid additive for cement resiliency**
(57) Abstract

A cement composition including: a hydraulic cement; at least a sufficient concentration of water to form a pumpable slurry with the hydraulic cement; a polymer selected from the group consisting of: (i) a homopolymer of one monomer selected from the group consisting of: N isopropylacrylamide, N propylacrylamide, and N,N diethylacrylamide; (ii) a copolymer consisting of two or more monomers selected from the group consisting of: N isopropylacrylamide, N propylacrylamide, and N,N diethylacrylamide; and (iii) a copolymer comprising: one or more first monomers selected from the group consisting of: N isopropylacrylamide, N propylacrylamide, N,N diethylacrylamide, and any combination thereof; one or more second monomers selected from the group consisting of: acrylamide, an acrylamide derivative other than one of the first monomers, methacrylamide, an N alkylmethacrylamide, N-methyl-N-vinylacetamide, N-vinylformamide, a vinylpyrrolidone, a vinylpyridine, N-vinylcaprolactam, N-methyl-N-vinylacetamide, a styrene sulfonic acid, a styrenesulfonate, a vinylsulfonic acid, a vinylulfonate, and any combination thereof.



LIQUID ADDITIVE FOR CEMENT RESILIENCY

CROSS-REFERENCE TO RELATED APPLICATIONS

Not applicable.

TECHNICAL FIELD

[0001] The disclosure is in the field of hydraulic cement compositions. Such compositions can be useful in producing crude oil or natural gas from subterranean formations, such as cementing of wells.

BACKGROUND

[0002] Prior materials used to modify the mechanical properties of set cement include elastomeric-based particles. Such elastomeric particulates primarily affect the Young's modulus and Poisson's ratio of a set cement.

[0003] Examples of such solid particulates include: LATEX 2000TM and LATEX 3000TM, which are very small elastomer particles (specific gravity about 1) suspended in an aqueous solution (about 50% by weight), and LAP-1TM, which is a solid particulate of a polyvinyl alcohol that is slightly crosslinked (specific gravity about 1.33), all of which are commercially available from Halliburton Energy Services, Inc. in Duncan, Oklahoma. Other examples include styrene-butadiene copolymer ("SBC") particulates (specific gravity about 1). SBC particulates are often provided as dry, solid materials that can be dry-blended.

[0004] Cement slurries usually have specific gravities in the range of about 1.44 (12 lb/gal) to about 2.28 (19 lb/gal). Because solid elastomeric materials such as SBC have a specific gravity lower than the specific gravities for common cement slurries, they tend to float to the surface rather than stay suspended in the cement slurry, resulting in cement slurry stability issues.

[0005] An elastomeric material can have a weighting agents, such as barite powder, incorporated into the matrix of the elastomeric material to increase the apparent specific gravity of a particulate formed with such a mixed material; however, twice as much of such a product (by weight) is required to meet the same active elastomer content.

GENERAL DESCRIPTION OF EMBODIMENTS

[0006] The disclosure provides a polymer can be included in a cement slurry to provide a set cement that has lower Young's Modulus values and, hence, is a more resilient set cement.

[0007] The polymer can be dissolved in an aqueous phase that can be included in a cement composition; however, upon heating, which can be, for example, due to downhole temperature conditions in a well, the dissolved polymer will precipitate to form solid particles. Due to this change from a liquid state to a solid state, there are no cement slurry stability issues relating to surface mixing of the dissolved polymer.

[0008] According to an embodiment of the disclosure, a hydraulic cement composition including: (A) a hydraulic cement; (B) at least a sufficient concentration of water to form a pumpable slurry with the hydraulic cement; and (C) a polymer selected from the group consisting of: (i) a homopolymer of one monomer selected from the group consisting of: *N*-isopropylacrylamide, *N*-propyl acrylamide, and *N,N*-diethyl acrylamide; (ii) a copolymer consisting of two or more monomers selected from the group consisting of: *N*-isopropylacrylamide, *N*-propyl acrylamide, and *N,N*-diethyl acrylamide; and (iii) a copolymer comprising: (a) one or more first monomers selected from the group consisting of: *N*-isopropylacrylamide, *N*-propyl acrylamide, *N,N*-diethyl acrylamide, and any combination thereof; and (b) one or more second monomers selected from the group consisting of: acrylamide, an acrylamide derivative other than one of the first monomers, methacrylamide, an *N*-alkyl methacrylamide, *N*-methyl-*N*-vinylacetamide, *N*-vinylformamide, a vinyl pyrrolidone, a vinyl pyridine, *N*-vinylcaprolactam, *N*-methyl-*N*-vinylacetamide, a styrene sulfonic acid, a styrene sulfonate, a vinyl sulfonic acid, a vinyl sulfonate, and any combination of the foregoing.

[0009] In cases where the setting temperature is greater than a lower critical solution temperature ("LCST") of the polymer, at least some of any such dissolved polymer will precipitate to increase the resiliency of the set cement.

[0010] According to an embodiment of the disclosure, a method of cementing in a well includes: (A) forming such a hydraulic cement composition according to this disclosure; and (B) introducing the hydraulic cement composition into a treatment zone of the well. In cases where the design temperature of the treatment zone in the well is greater than a lower critical solution temperature ("LCST") of the polymer, at least some of any such dissolved polymer will precipitate to increase the resiliency of the set cement.

[0011] These and other embodiments of the disclosure will be apparent to one skilled in the art upon reading the following detailed description. While the disclosure is susceptible to various modifications and alternative forms, specific embodiments thereof will be described in detail and shown by way of example. It should be understood, however, that it is not intended to limit the disclosure to the particular forms disclosed.

BRIEF DESCRIPTION OF THE DRAWING

[0012] The accompanying drawing is incorporated into the specification to help illustrate examples according to a presently preferred embodiment of the disclosure.

[0013] **Figure 1** is a graph showing the setting of a control cement without any NIPAM/DMAC polymer.

[0014] **Figure 2** is a graph showing the setting of a cement having 1.82 gal/sack (7.5 eq. % bwoc) low molecular weight NIPAM/DMAC copolymer.

**DETAILED DESCRIPTION OF PRESENTLY PREFERRED EMBODIMENTS
AND BEST MODE**

Definitions and Usages

General Interpretation

[0015] The words or terms used herein have their plain, ordinary meaning in the field of this disclosure, except to the extent explicitly and clearly defined in this disclosure or unless the specific context otherwise requires a different meaning.

[0016] The words “comprising,” “containing,” “including,” “having,” and all grammatical variations thereof are intended to have an open, non-limiting meaning. For example, a composition comprising a component does not exclude it from having additional components, an apparatus comprising a part does not exclude it from having additional parts, and a method having a step does not exclude it having additional steps. When such terms are used, the compositions, apparatuses, and methods that “consist essentially of” or “consist of” the specified components, parts, and steps are specifically included and disclosed. As used herein, the words “consisting essentially of,” and all grammatical variations thereof are intended to limit the scope of a claim to the specified materials or steps and those that do not materially affect the basic and novel characteristic(s) of the claimed invention.

[0017] The indefinite articles “a” or “an” mean one or more than one of the component, part, or step that the article introduces.

[0018] Whenever a numerical range of degree or measurement with a lower limit and an upper limit is disclosed, any number and any range falling within the range is also intended to be specifically disclosed. For example, every range of values (in the form “from a to b,” or “from about a to about b,” or “from about a to b,” “from approximately a to b,” and any similar expressions, where “a” and “b” represent numerical values of degree or measurement) is to be understood to set forth every number and range encompassed within the broader range of values.

[0019] Terms such as “first,” “second,” “third,” etc. may be assigned arbitrarily and are merely intended to differentiate between two or more components, parts, or steps that are otherwise similar or corresponding in nature, structure, function, or action. For example, the words “first” and “second” serve no other purpose and are not part of the name or description of

the following name or descriptive terms. The mere use of the term “first” does not require that there be any “second” similar or corresponding component, part, or step. Similarly, the mere use of the word “second” does not require that there be any “first” or “third” similar or corresponding component, part, or step. Further, it is to be understood that the mere use of the term “first” does not require that the element or step be the very first in any sequence, but merely that it is at least one of the elements or steps. Similarly, the mere use of the terms “first” and “second” does not necessarily require any sequence. Accordingly, the mere use of such terms does not exclude intervening elements or steps between the “first” and “second” elements or steps, etc.

Oil and Gas Reservoirs

[0020] In the context of production from a well, “oil” and “gas” are understood to refer to crude oil and natural gas, respectively. Oil and gas are naturally occurring hydrocarbons in certain subterranean formations.

[0021] A “subterranean formation” is a body of rock that has sufficiently distinctive characteristics and is sufficiently continuous for geologists to describe, map, and name it.

[0022] A subterranean formation having a sufficient porosity and permeability to store and transmit fluids is sometimes referred to as a “reservoir.”

[0023] A subterranean formation containing oil or gas may be located under land or under the seabed off shore. Oil and gas reservoirs are typically located in the range of a few hundred feet (shallow reservoirs) to a few tens of thousands of feet (ultra-deep reservoirs) below the surface of the land or seabed.

Well Servicing and Fluids

[0024] To produce oil or gas from a reservoir, a wellbore is drilled into a subterranean formation, which may be the reservoir or adjacent to the reservoir. Typically, a wellbore of a well must be drilled hundreds or thousands of feet into the earth to reach a hydrocarbon-bearing formation.

[0025] Generally, well services include a wide variety of operations that may be performed in oil, gas, geothermal, or water wells, such as drilling, cementing, completion, and intervention. Well services are designed to facilitate or enhance the production of desirable fluids such as oil or gas from or through a subterranean formation. A well service usually involves introducing a fluid into a well.

[0026] Drilling is the process of drilling the wellbore. After a portion of the wellbore is drilled, sections of steel pipe, referred to as casing, which are slightly smaller in diameter than the borehole, are placed in at least the uppermost portions of the wellbore. The casing provides structural integrity to the newly drilled borehole.

[0027] Cementing is a common well operation. For example, hydraulic cement compositions can be used in cementing operations in which a string of pipe, such as casing or liner, is cemented in a wellbore. The cement stabilizes the pipe in the wellbore and prevents undesirable migration of fluids along the annulus between the wellbore and the outside of the casing or liner from one zone along the wellbore to the next. Where the wellbore penetrates into a hydrocarbon-bearing zone of a subterranean formation, the casing can later be perforated to allow fluid communication between the zone and the wellbore. The cemented casing also enables subsequent or remedial separation or isolation of one or more production zones of the wellbore by using downhole tools, such as packers or plugs, or by using other techniques, such as forming sand plugs or placing cement in the perforations. Hydraulic cement compositions can also be utilized in intervention operations, such as in plugging highly permeable zones, or fractures in zones, that may be producing too much water, plugging cracks or holes in pipe strings, and the like.

[0028] Completion is the process of making a well ready for production or injection. This principally involves preparing a zone of the wellbore to the required specifications, running in the production tubing and associated downhole equipment, as well as perforating and stimulating as required.

[0029] Intervention is any operation carried out on a well during or at the end of its productive life that alters the state of the well or well geometry, provides well diagnostics, or manages the production of the well.

[0030] Drilling, cementing, completion, and intervention operations can include various types of treatments that are commonly performed on a well or subterranean formation. Among other types of treatments, cementing or remedial cementing may be useful treatments as part of such operations.

Wells

[0031] A “well” includes a wellhead and at least one wellbore from the wellhead penetrating the earth. The “wellhead” is the surface termination of a wellbore, which surface may be on land or on a seabed.

[0032] A “well site” is the geographical location of a wellhead of a well. It may include related facilities, such as a tank battery, separators, compressor stations, heating or other equipment, and fluid pits. If offshore, a well site can include a platform.

[0033] The “wellbore” refers to the drilled hole, including any cased or uncased portions of the well or any other tubulars in the well. The “borehole” usually refers to the inside wellbore wall, that is, the rock surface or wall that bounds the drilled hole. A wellbore can have portions that are vertical, horizontal, or anything in between, and it can have portions that are straight, curved, or branched. As used herein, “uphole,” “downhole,” and similar terms are relative to the direction of the wellhead, regardless of whether a wellbore portion is vertical or horizontal.

[0034] As used herein, introducing “into a well” means introducing at least into and through the wellhead. According to various techniques known in the art, tubulars, equipment, tools, or fluids can be directed from the wellhead into any desired portion of the wellbore.

[0035] As used herein, the word “tubular” means any kind of structural body in the general form of a tube. Examples of tubulars in oil wells include, but are not limited to, a drill pipe, a casing, a tubing string, a line pipe, and a transportation pipe.

[0036] As used herein, the term “annulus” means the space between two generally cylindrical objects, one inside the other. The objects can be concentric or eccentric. Without limitation, one of the objects can be a tubular and the other object can be an enclosed conduit. The enclosed conduit can be a wellbore or borehole or it can be another tubular. The following

are some non-limiting examples illustrating some situations in which an annulus can exist. Referring to an oil, gas, or water well, in an open hole well, the space between the outside of a tubing string and the borehole of the wellbore is an annulus. In a cased hole, the space between the outside of the casing and the borehole is an annulus. In addition, in a cased hole there may be an annulus between the outside cylindrical portion of a tubular, such as a production tubing string, and the inside cylindrical portion of the casing. An annulus can be a space through which a fluid can flow or it can be filled with a material or object that blocks fluid flow, such as a packing element. Unless otherwise clear from the context, as used herein an “annulus” is a space through which a fluid can flow.

[0037] A fluid can be, for example, a drilling fluid, a setting composition, a treatment fluid, or a spacer fluid.

[0038] As used herein, the word “treatment” refers to any treatment for changing a condition of a portion of a wellbore or a subterranean formation adjacent a wellbore; however, the word “treatment” does not necessarily imply any particular treatment purpose. A treatment usually involves introducing a fluid for the treatment, in which case it may be referred to as a treatment fluid, into a well. As used herein, a “treatment fluid” is a fluid used in a treatment. The word “treatment” in the term “treatment fluid” does not necessarily imply any particular treatment or action by the fluid.

[0039] As used herein, the terms spacer fluid, wash fluid, and inverter fluid can be used interchangeably. A spacer fluid is a fluid used to physically separate one special-purpose fluid from another. It may be undesirable for one special-purpose fluid to mix with another used in the well, so a spacer fluid compatible with each is used between the two. A spacer fluid is usually used when changing between fluids used in a well.

[0040] In the context of a well or wellbore, a “portion” or “interval” refers to any downhole portion or interval along the length of a wellbore.

[0041] A “zone” refers to an interval of rock along a wellbore that is differentiated from uphole and downhole zones based on hydrocarbon content or other features, such as permeability, composition, perforations or other fluid communication with the wellbore, faults, or fractures. A zone of a wellbore that penetrates a hydrocarbon-bearing zone that is capable of

producing hydrocarbon is referred to as a “production zone.” A “treatment zone” refers to an interval of rock along a wellbore into which a fluid is directed to flow from the wellbore. As used herein, “into a treatment zone” means into and through the wellhead and, additionally, through the wellbore and into the treatment zone.

[0042] Generally, the greater the depth of the formation, the higher the static temperature and pressure of the formation. Initially, the static pressure equals the initial pressure in the formation before production. After production begins, the static pressure approaches the average reservoir pressure.

[0043] A “design” refers to the estimate or measure of one or more parameters planned or expected for a particular fluid or stage of a well service or treatment. For example, a fluid can be designed to have components that provide a minimum density or viscosity for at least a specified time under expected downhole conditions. A well service may include design parameters such as fluid volume to be pumped, required pumping time for a treatment, or the shear conditions of the pumping.

[0044] The term “design temperature” refers to an estimate or measurement of the actual temperature at the downhole environment during the time of a treatment. For example, the design temperature for a well treatment takes into account not only the bottom hole static temperature (“BHST”), but also the effect of the temperature of the fluid on the BHST during treatment. The design temperature for a fluid is sometimes referred to as the bottom hole circulation temperature (“BHCT”). Because fluids may be considerably cooler than BHST, the difference between the two temperatures can be quite large. Ultimately, if left undisturbed a subterranean formation will return to the BHST.

Phases, Physical States, and Materials

[0045] As used herein, “phase” is used to refer to a substance having a chemical composition and physical state that is distinguishable from an adjacent phase of a substance having a different chemical composition or a different physical state.

[0046] As used herein, if not otherwise specifically stated, the physical state or phase of a substance (or mixture of substances) and other physical properties are determined at a

temperature of 77 °F (25 °C) and a pressure of 1 atmosphere (Standard Laboratory Conditions) without applied shear.

[0047] The word “material” refers to the substance, constituted of one or more phases, of a physical entity or object. Rock, water, air, metal, cement slurry, sand, and wood are all examples of materials. The word “material” can refer to a single phase of a substance on a bulk scale (larger than a particle) or a bulk scale of a mixture of phases, depending on the context.

Particles and Particulates

[0048] As used herein, a “particle” refers to a body having a finite mass and sufficient cohesion such that it can be considered as an entity but having relatively small dimensions. A particle can be of any size ranging from molecular scale to macroscopic, depending on context.

[0049] A particle can be in any physical state. For example, a particle of a substance in a solid state can be as small as a few molecules on the scale of nanometers up to a large particle on the scale of a few millimeters, such as large grains of sand. Similarly, a particle of a substance in a liquid state can be as small as a few molecules on the scale of nanometers up to a large drop on the scale of a few millimeters.

[0050] As used herein, particulate or particulate material refers to matter in the physical form of distinct particles in a solid or liquid state (which means such an association of a few atoms or molecules). As used herein, a particulate is a grouping of particles having similar chemical composition and particle size ranges anywhere in the range of about 0.5 micrometer (500 nm), for example, microscopic clay particles, to about 3 millimeters, for example, large grains of sand.

[0051] A particulate can be of solid or liquid particles. As used herein, however, unless the context otherwise requires, particulate refers to a solid particulate.

[0052] As used herein, “particle density” or “true density” means the density of a particulate is the density of the individual particles that make up the particulate, in contrast to the bulk density, which measures the average density of a large volume of the powder in a specific medium (usually air). The particle density is a relatively well-defined quantity, as it is not dependent on the degree of compaction of the solid, whereas the bulk density has different values

depending on whether it is measured in the freely settled or compacted state (tap density). However, a variety of definitions of particle density are available, which differ in terms of whether pores are included in the particle volume, and whether voids are included. As used herein, particle density includes the apparent density of a particle having any pores or voids into which water does not penetrate.

Dispersions

[0053] A dispersion is a system in which particles of a substance of one chemical composition and physical state are dispersed in another substance of a different chemical composition or physical state. In addition, phases can be nested. If a substance has more than one phase, the most external phase is referred to as the continuous phase of the substance as a whole, regardless of the number of different internal phases or nested phases.

[0054] A dispersion can be classified in different ways, including, for example, based on the size of the dispersed particles, the uniformity or lack of uniformity of the dispersion, and, if a fluid, by whether or not precipitation occurs.

[0055] A dispersion is considered to be heterogeneous if the dispersed particles are not dissolved and are greater than about 1 nanometer in size. (For reference, the diameter of a molecule of toluene is about 1 nm and a molecule of water is about 0.3 nm).

[0056] Heterogeneous dispersions can have gas, liquid, or solid as an external phase. For example, in a case where the dispersed-phase particles are liquid in an external phase that is another liquid, this kind of heterogeneous dispersion is more particularly referred to as an emulsion. A solid dispersed phase in a continuous liquid phase is referred to as a sol, suspension, or slurry, partly depending on the size of the dispersed solid particulate.

[0057] A dispersion is considered to be homogeneous if the dispersed particles are dissolved in solution or the particles are less than about 1 nanometer in size. Even if not dissolved, a dispersion is considered to be homogeneous if the dispersed particles are less than about 1 nanometer in size.

[0058] Heterogeneous dispersions can be further classified based on the dispersed particle size.

[0059] A heterogeneous dispersion is a “suspension” where the dispersed particles are larger than about 50 micrometers. Such particles can be seen with a microscope, or if larger than about 50 micrometers (0.05 mm), with the unaided human eye. The dispersed particles of a suspension in a liquid external phase may eventually separate on standing, for example, settle in cases where the particles have a higher density than the liquid phase. Suspensions having a liquid external phase are essentially unstable from a thermodynamic point of view; however, they can be kinetically stable over a long period depending on temperature and other conditions.

[0060] A heterogeneous dispersion is a “slurry” where the dispersed particles are larger than about 50 micrometers, which can be seen with the unaided human eye. A hydraulic cement dispersed in water is usually considered to be a slurry.

Solutions and Hydratability or Solubility

[0061] A solution is a special type of homogeneous mixture. A solution is considered homogeneous: (a) because the ratio of solute to solvent is the same throughout the solution; and (b) because solute will never settle out of solution, even under powerful centrifugation, which is due to intermolecular attraction between the solvent and the solute. An aqueous solution, for example, saltwater, is a homogenous solution in which water is the solvent and salt is the solute.

[0062] One may also refer to the solvated state, in which a solute ion or molecule is complexed by solvent molecules. A chemical that is dissolved in solution is in a solvated state. The solvated state is distinct from dissolution and solubility. Dissolution is a kinetic process, and is quantified by its rate. Solubility quantifies the concentration of the solute at which there is dynamic equilibrium between the rate of dissolution and the rate of precipitation of the solute. Dissolution and solubility can be dependent on temperature and pressure, and may be dependent on other factors, such as salinity or pH of an aqueous phase.

[0063] As referred to herein, “hydratable” means capable of being hydrated by contacting the hydratable material with water. Regarding a hydratable material that includes a polymer, this means, among other things, to associate sites on the polymer with water molecules and to unravel and extend the polymer chain in the water.

[0064] The term “solution” is intended to include not only true molecular solutions but also dispersions of a polymer wherein the polymer is so highly hydrated as to cause the dispersion to be visually clear and having essentially no particulate matter visible to the unaided eye. The term “soluble” is intended to have a meaning consistent with these meanings of solution.

[0065] As used herein, a substance is considered to be “soluble” in a liquid if at least 10 grams of the substance can be hydrated or dissolved in one liter of the liquid when tested at 60 °F (15 °C) and 1 atmosphere pressure for 2 hours, considered to be “insoluble” if less than 1 gram per liter, and considered to be “sparingly soluble” for intermediate solubility values.

[0066] As will be appreciated by a person of skill in the art, the hydratability, dispersibility, or solubility of a substance in water can be dependent on the salinity, pH, or other substances in the water. Accordingly, the salinity, pH, and additive selection of the water can be modified to facilitate the hydratability, dispersibility, or solubility of a substance in aqueous solution. To the extent not specified, the hydratability, dispersibility, or solubility of a substance in water is determined in deionized water, at neutral pH, and without any other additives.

[0067] As used herein, the term “polar” means having a dielectric constant greater than 30. The term “relatively polar” means having a dielectric constant greater than about 2 and less than about 30. “Non-polar” means having a dielectric constant less than 2.

Fluids

[0068] A fluid can be a homogeneous or heterogeneous. In general, a fluid is an amorphous substance that is or has a continuous phase of particles that are smaller than about 1 micrometer that tends to flow and to conform to the outline of its container.

[0069] Examples of fluids are gases and liquids. A gas (in the sense of a physical state) refers to an amorphous substance that has a high tendency to disperse (at the molecular level) and a relatively high compressibility. A liquid refers to an amorphous substance that has little tendency to disperse (at the molecular level) and relatively high incompressibility. The tendency to disperse is related to Intermolecular Forces (also known as van der Waal’s Forces). (A continuous mass of a particulate, for example, a powder or sand, can tend to flow as a fluid

depending on many factors such as particle size distribution, particle shape distribution, the proportion and nature of any wetting liquid or other surface coating on the particles, and many other variables. Nevertheless, as used herein, a fluid does not refer to a continuous mass of particulate as the sizes of the solid particles of a mass of a particulate are too large to be appreciably affected by the range of Intermolecular Forces.)

[0070] Every fluid inherently has at least a continuous phase. A fluid can have more than one phase. The continuous phase of a treatment fluid is a liquid under Standard Laboratory Conditions. For example, a fluid can be in the form of a suspension (larger solid particles dispersed in a liquid phase), such as a slurry, an emulsion (liquid particles dispersed in another liquid phase), or a foam (a gas phase dispersed in a liquid phase).

Apparent Viscosity of a Fluid

[0071] Viscosity is a measure of the resistance of a fluid to flow. In everyday terms, viscosity is “thickness” or “internal friction.” Therefore, pure water is “thin,” having a relatively low viscosity whereas honey is “thick,” having a relatively higher viscosity. Put simply, the less viscous the fluid is, the greater its ease of movement (fluidity). More precisely, viscosity is defined as the ratio of shear stress to shear rate.

[0072] A fluid moving along solid boundary will incur a shear stress on that boundary. The no-slip condition dictates that the speed of the fluid at the boundary (relative to the boundary) is zero, but at some distance from the boundary, the flow speed must equal that of the fluid. The region between these two points is named the boundary layer.

[0073] A Newtonian fluid (named after Isaac Newton) is a fluid for which stress versus strain rate curve is linear and passes through the origin. The constant of proportionality is known as the viscosity. Examples of Newtonian fluids include water and most gases. Newton’s law of viscosity is an approximation that holds for some substances but not others.

[0074] Non-Newtonian fluids exhibit a more complicated relationship between shear stress and velocity gradient (i.e., shear rate) than simple linearity. Therefore, there exist a number of forms of non-Newtonian fluids. Shear thickening fluids have an apparent viscosity that increases with increasing the rate of shear. Shear thinning fluids have a viscosity that

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

[0075] Most fluids are non-Newtonian fluids. Accordingly, the apparent viscosity of a fluid applies only under a particular set of conditions including shear stress versus shear rate, which must be specified or understood from the context. As used herein, a reference to viscosity is actually a reference to an apparent viscosity. Apparent viscosity is commonly expressed in units of mPa·s or centipoise (cP), which are equivalent.

Cement and Cement Compositions

[0076] As used herein, the term “set” means the process of becoming solid or hard by curing.

[0077] In the most general sense of the word, a “cement” is a binder, that is, a substance that sets. As used herein, “cement” refers to an inorganic cement that, when mixed with water, will begin to set and harden into a concrete material.

[0078] As used herein, a “cement composition” is a material including at least one inorganic cement. A cement composition can also include additives. Some cement compositions can include water or be mixed with water. Depending on the type of cement, the chemical proportions, when a cement composition is mixed with water it can begin setting to form a solid material.

[0079] A cement can be characterized as non-hydraulic or hydraulic.

[0080] Hydraulic cements (for example, Portland cement) harden because of hydration, chemical reactions that occur independently of the mixture’s water content; they can harden even underwater or when constantly exposed to wet weather. The chemical reaction that results when the dry cement powder is mixed with water produces hydrates that have extremely low solubility in water. The cement composition sets by a hydration process, and it passes through a gel phase to solid phase.

[0081] More particularly, Portland cement is formed from a clinker such as a clinker according to the European Standard EN197-1: “Portland cement clinker is a hydraulic material which shall consist of at least two-thirds by mass of calcium silicates ($3 \text{ CaO} \cdot \text{SiO}_2$ and $2 \text{ CaO} \cdot \text{SiO}_2$), the remainder consisting of aluminium- and iron-containing clinker phases and other compounds. The ratio of CaO to SiO_2 shall not be less than 2.0. The magnesium oxide content (MgO) shall not exceed 5.0% by mass.” The American Society of Testing Materials (“ASTM”) standard “C 150” defines Portland cement as “hydraulic cement (cement that not only hardens by reacting with water but also forms a water-resistant product) produced by pulverizing clinkers consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate as an inter ground addition.” In addition, Portland cements typically have a ratio of CaO to SiO_2 of less than 4.0.

[0082] Clinkers are nodules (diameters about 0.2 inch to about 1.0 inch [about 5 mm to about 25 mm]) of a sintered material that is produced when a raw mixture of predetermined composition is heated to high temperature.

[0083] Portland cement clinker is made by heating to sintering temperature a mixture of raw materials, which is about 1450 °C for modern cements. The alumina and iron oxide are present as a flux and contribute little to the strength.

[0084] The American Society for Testing and Materials (ASTM) has established a set of standards for a Portland cement to meet to be considered an ASTM cement. These standards include Types I, II, III, IV, and V.

[0085] The American Petroleum Institute (API) has established a set of standards that a Portland cement must meet to be considered an API cement. The standards include Classes A, B, C, D, E, F, G, H, I, and J.

[0086] A blended cement is a hydraulic cement produced by intergrinding Portland cement clinker with other materials, by blending Portland cement with other materials, or by a combination of intergrinding and blending.

Cementing and Other Uses for Cement Compositions

[0087] During well completion, it is common to introduce a cement composition into an annulus in the wellbore. For example, in a cased hole, the cement composition is placed into and allowed to set in the annulus between the wellbore and the casing in order to stabilize and secure the casing in the wellbore. After setting, the set cement composition should have a low permeability. Consequently, oil or gas can be produced in a controlled manner by directing the flow of oil or gas through the casing and into the wellhead.

[0088] Cement compositions can also be used, for example, in well-plugging operations or gravel-packing operations. Cement compositions can also be used to control fluid loss or migration in zones.

[0089] During placement of a cement composition, it is necessary for the cement composition to remain pumpable during introduction into the subterranean formation or the well and until the cement composition is situated in the portion of the subterranean formation or the well to be cemented. After the cement composition has reached the portion of the well to be cemented, the cement composition ultimately sets. A cement composition that thickens too quickly while being pumped can damage pumping equipment or block tubing or pipes, and a cement composition that sets too slowly can cost time and money while waiting for the cement composition to set.

Pumping Time and Thickening Time

[0090] As used herein, the “pumping time” is the total time required for pumping a hydraulic cementing composition into a desired portion or zone of the well in a cementing operation plus a safety factor.

[0091] As used herein, the “thickening time” is how long it takes for a cement composition to become unpumpable at a specified temperature and specified pressure. The pumpability of a cement composition is related to the consistency of the composition. The consistency of a cement composition is measured in Bearden units of consistency (Bc), a dimensionless unit with no direct conversion factor to the more common units of viscosity. As used herein, a setting fluid is considered to be “pumpable” so long as the fluid has an apparent

viscosity less than 30,000 mPa•s (cP) (independent of any gel characteristic) or a consistency of less than 70 Bc. A setting fluid becomes “unpumpable” when the consistency of the composition reaches at least 70 Bc.

[0092] As used herein, the consistency of a cement composition is measured according to ANSI/API Recommended Practice 10B-2 as follows. The cement composition is mixed and then placed in the test cell of a High-Temperature, High-Pressure (HTHP) consistometer, such as a FANN™ Model 290 or a CHANDLER™ Model 8340. The cement composition is tested in the HTHP consistometer at the specified temperature and pressure. Consistency measurements are taken continuously until the consistency of the cement composition exceeds 70 Bc.

[0093] Of course, the thickening time should be greater than the pumping time for a cementing operation.

Setting and Compressive Strength

[0094] Depending on the composition and the conditions, it can take just a few minutes up to 72 hours or longer for some cement compositions to initially set. A cement composition sample that is at least initially set is suitable for destructive compressive strength testing.

[0095] Compressive strength is defined as the capacity of a material to withstand axially directed pushing forces. The compressive strength a setting composition attains is a function of both curing time and temperature, among other things.

[0096] The compressive strength of a cement composition can be used to indicate whether the cement composition has set. As used herein, a cement composition is considered “initially set” when the cement composition has developed a compressive strength of 50 psi using the non-destructive compressive strength method. As used herein, the “initial setting time” is the difference in time between when the cement is mixed with water and when the cement composition is initially set. Some cement compositions can continue to develop a compressive strength greater than 50 psi over the course of several days. The compressive strength of certain kinds of cement compositions can reach over 10,000 psi.

[0097] Compressive strength is typically measured at a specified time after the cement composition has been mixed and at a specified temperature and pressure conditions. If not

otherwise stated, the setting and the initial setting time is determined at a temperature of 212 °F and an atmospheric pressure of 3,000 psi. Compressive strength can also be measured at a specific time and temperature after the cement composition has been mixed, for example, in the range of about 24 to about 72 hours at a design temperature and pressure, for example, a temperature of 212 °F and 3,000 psi. According to ANSI/API Recommended Practice 10B-2, compressive strength can be measured by either a destructive method or non-destructive method.

[0098] The destructive method mechanically tests the strength of cement composition samples at various points in time by crushing the samples in a compression-testing machine. The destructive method is performed as follows. The cement composition is mixed and then cured. The cured cement composition sample is placed in a compressive strength testing device, such as a Super L Universal testing machine model 602, available from Tinius Olsen, Horsham in Pennsylvania, USA. According to the destructive method, the compressive strength is calculated as the force required to break the sample divided by the smallest cross-sectional area in contact with the load-bearing plates of the compression device. The actual compressive strength is reported in units of pressure, such as pound-force per square inch (psi) or megapascals (MPa).

[0099] The non-destructive method continually measures a correlated compressive strength of a cement composition sample throughout the test period by utilizing a non-destructive sonic device such as an Ultrasonic Cement Analyzer (UCA) available from Fann Instruments in Houston, TX. As used herein, the “compressive strength” of a cement composition is measured utilizing an Ultrasonic Cement Analyzer as follows. The cement composition is mixed. The cement composition is placed in an Ultrasonic Cement Analyzer, in which the cement composition is heated to the specified temperature and pressurized to the specified pressure. The UCA continually measures the transit time of the acoustic signal through the sample. The UCA device contains preset algorithms that correlate transit time through the sample to compressive strength. The UCA reports the compressive strength of the cement composition in units of pressure, such as psi or megapascals (MPa).

Young's Modulus (Elastic Modulus)

[0100] Young's modulus, named after Thomas Young, is also known as the elastic modulus. It is a measure of the stiffness of an elastic material. It is defined as the ratio of the stress along an axis over the strain along that axis in the range of stress in which Hooke's law holds. The slope of the stress-strain curve at any point is called the tangent modulus. The tangent modulus of the initial, linear portion of a stress-strain curve is called Young's modulus. It can be experimentally determined from the slope of a stress-strain curve created during tensile tests conducted on a sample of the material. Young's modulus is the ratio of stress (which has units of pressure) to strain (which is dimensionless); therefore, Young's modulus has units of pressure.

Poisson's Ratio

[0101] Poisson's ratio, named after Siméon Poisson, is the negative ratio of transverse to axial strain. When a material is compressed in one direction, it usually tends to expand in the other two directions perpendicular to the direction of compression. This phenomenon is called the Poisson effect. Poisson's ratio is a measure of this effect. The Poisson ratio is the ratio of the fraction (or percent) of expansion divided by the fraction (or percent) of compression, for small values of these changes. Conversely, if the material is stretched rather than compressed, it usually tends to contract in the directions transverse to the direction of stretching. In this case, the Poisson ratio will be the ratio of relative contraction to relative stretching, and will have the same value as above.

Cement Testing Conditions

[0102] As used herein, if any test (for example, thickening time or compressive strength, requires the step of mixing the setting composition, cement composition, or the like, then the mixing step is performed according to ANSI/API Recommended Practice 10B-2 as follows. Any of the ingredients that are a dry particulate substance are pre-blended. The liquid is added to a mixing container and the container is then placed on a mixer base. For example, the mixer can be a Lightning Mixer. The motor of the base is then turned on and maintained at

about 4,000 revolutions per minute (rpm). The pre-blended dry ingredients are added to the container at a uniform rate in not more than 15 seconds (s). After all the dry ingredients have been added to the liquid ingredients in the container, a cover is then placed on the container, and the composition is mixed at 12,000 rpm (+/- 500 rpm) for 35 s (+/- 1 s). It is to be understood that the composition is mixed under Standard Laboratory Conditions (about 77 °F and about 1 atmosphere pressure).

[0103] It is also to be understood that if any test (for example, thickening time or compressive strength or permeability) specifies the test be performed at a specified temperature and possibly a specified pressure, then the temperature and pressure of the cement composition is ramped up to the specified temperature and pressure after being mixed at ambient temperature and pressure. For example, the cement composition can be mixed at 77 °F and then placed into the testing apparatus and the temperature of the cement composition can be ramped up to the specified temperature. As used herein, the rate of ramping up the temperature is in the range of about 3 °F/min to about 5 °F/min. After the cement composition is ramped up to the specified temperature and possibly pressure, the cement composition is maintained at that temperature and pressure for the duration of the testing.

[0104] As used herein, if any test (for example, compressive strength or permeability) requires the step of “curing the cement composition” or the like, then the curing step is performed according to ANSI/API Recommended Practice 10B-2 as follows. After the cement composition has been mixed, it is poured into a curing mold. The curing mold is placed into a pressurized curing chamber and the curing chamber is maintained at a temperature of 212 °F and a pressure of 3000 psi. The cement composition is allowed to cure for the length of time necessary for the composition to set. After the composition has set, the curing mold is placed into a water cooling bath until the cement composition sample is tested.

Cement Retarders

[0105] As used herein, a “retarder” is a chemical agent used to increase the thickening time of a cement composition. The need for retarding the thickening time of a cement composition tends to increase with depth of the zone to be cemented due to the greater time

required to complete the cementing operation and the effect of increased temperature on the setting of the cement. A longer thickening time at the design temperature allows for a longer pumping time that may be required.

Other Cement Additives

[0106] Cement compositions can contain other additives, including but not limited to resins, latex, stabilizers, silica, microspheres, aqueous superabsorbers, viscosifying agents, suspending agents, dispersing agents, salts, accelerants, surfactants, retardants, defoamers, high-density materials, low-density materials, fluid-loss control agents, elastomers, vitrified shale, gas migration control additives, formation conditioning agents, or other additives or modifying agents, or combinations thereof.

[0107] An example of an additive is a high-density additive. As used herein, a “high-density” additive is an additive that has a density greater than 3 g/cm³. Some metal oxides can be used as a high-density additive. As used herein, a “metal oxide” is a metal cation or transition metal cation with an oxide anion. Examples of metal oxides include, but are not limited to, iron oxide (Fe₂O₃) and manganese oxide (Mn₃O₄). A commercially available example of an iron oxide high-density additive is HI-DENSE™ and an example of a commercially available manganese oxide is MICROMAX™, both available from Halliburton Energy Services, Inc. in Duncan, Oklahoma.

[0108] For example, MICROMAX™ weight additive increases slurry density with hausmannite ore ground to an average particle size of 5 microns. Unlike most weighting materials, MICROMAX™ weight additive remains in suspension when added directly to mixing water. MICROMAX™ weight additive can be used at bottomhole circulating temperatures between 80 °F and 500 °F (27 °C to 260 °C). In deep wells with high temperatures and pressures, MICROMAX™ weight additive can help restrain formation pressures and improve mud displacement. Additive concentrations depend on the slurry weight designed for individual wells. Because of the fine-ground ore in MICROMAX™ weight additive, higher concentrations of retarders might be required to achieve the thickening times provided by other types of weight additives. Slurries of cement compositions containing MICROMAX™ weight additive might

also require the addition of dispersants. MICROMAX™ weight additive is commercially available from Halliburton Energy Services, Inc. in Duncan, Oklahoma.

[0109] Some oil and gas wells can have a corrosive environment. As used herein, a “corrosive environment” is an environment containing corrosive materials. Examples of corrosive materials include, but are not limited to, liquids with a pH below 5, acid gas, or fluids containing dissolved acid gas. As used herein, the term “acid gas” means any gas that can mix with water to form an acidic solution having a pH below 5. The most common acid gases are hydrogen sulfide (H₂S) and carbon dioxide (CO₂). For example, CO₂ reacts with water to form carbonic acid in an aqueous solution.

[0110] A cement composition that contains a metal oxide, high-density additive is prone to corrosion if introduced into a well having a corrosive environment. For example, after the cement composition has set in the portion of the well, the corrosive materials in the well can corrode a portion of the cement composition. Consequently, for example, oil or gas can flow more easily through the annulus and it can be more difficult to produce oil or gas in a controlled manner through the casing. Moreover, as the permeability of the set composition increases, the corrosive materials can flow through the set composition and come in contact with the casing. The corrosive materials can then corrode portions of the casing. Moreover, if the set cement composition comes into contact with corrosive materials, some of the metal oxide of the cement composition can dissolve out of the composition and then precipitate elsewhere to plug up other areas of the well. As a result, it can become more difficult to produce oil or gas.

General Measurement Terms

[0111] Unless otherwise specified or unless the context otherwise clearly requires, any ratio or percentage means by weight.

[0112] Unless otherwise specified or unless the context otherwise clearly requires, the phrase “by weight of the water” means the weight of the water of an aqueous phase of the fluid without the weight of any viscosity-increasing agent, dissolved salt, suspended particulate, or other materials or additives that may be present in the water.

[0113] If there is any difference between U.S. or Imperial units, U.S. units are intended.

[0114] As used herein, a “sack” (“sk”) is an amount that weighs 94 pounds (94 lb/sk).

[0115] As used herein, the conversion between gallon per sack (gal/sk) and percent by weight of cement (% bwoc) is $1 \text{ gal/sk} = 3.96\% \text{ bwoc}$.

[0116] The conversion between pound per gallon (lb/gal or ppg) and kilogram per cubic meter (kg/m^3) is: $1 \text{ lb/gal} = (0.4536 \text{ kg/lb}) \times (\text{gal}/0.003785 \text{ m}^3) = 120 \text{ kg/m}^3$.

[0117] The conversion between pound per square foot (lb/ft^2) and kilogram per square meter (kg/m^2) is: $1 \text{ lb/ft}^2 = 4.9 \text{ kg/m}^2$.

General Approach

[0118] As stated above, this disclosure provides a polymer that can be included in a cement slurry to provide a set cement that has a lower Young's Modulus value and, hence, is a more resilient set cement.

[0119] The polymer can be dissolved in an aqueous phase that can be included in a cement composition; however, upon heating, which can be, for example, due to downhole temperature conditions in a well, the dissolved polymer will precipitate to form solid particles. Due to this change from a liquid state to a solid state, there are no cement slurry stability issues relating to surface mixing of the dissolved polymer.

[0120] As used herein, unless the context otherwise requires, a “polymer” or “polymeric material” includes homopolymers, copolymers, terpolymers, etc. In addition, the term “copolymer” as used herein is not limited to the combination of polymers having two monomeric units, but includes any combination of monomeric units, for example, terpolymers, tetrapolymers, etc.

[0121] According to an embodiment of the disclosure, a hydraulic cement composition is provided, the composition including: (A) a hydraulic cement; (B) at least a sufficient concentration of water to form a pumpable slurry with the hydraulic cement; and (C) a polymer selected from the group consisting of: (i) a homopolymer of one monomer selected from the group consisting of: *N*-isopropylacrylamide, *N*-propyl acrylamide, and *N,N*-diethyl acrylamide; (ii) a copolymer consisting of two or more monomers selected from the group consisting of: *N*-isopropylacrylamide, *N*-propyl acrylamide, and *N,N*-diethyl acrylamide; and (iii) a copolymer comprising: (a) one or more first monomers selected from the group consisting of:

N-isopropylacrylamide, *N*-propyl acrylamide, *N,N*-diethyl acrylamide, and any combination thereof; and (b) one or more second monomers selected from the group consisting of: acrylamide, an acrylamide derivative other than one of the first monomers, methacrylamide, an *N*-alkyl methacrylamide, *N*-methyl-*N*-vinylacetamide, *N*-vinylformamide, a vinyl pyrrolidone, a vinyl pyridine, *N*-vinylcaprolactam, *N*-methyl-*N*-vinylacetamide, a styrene sulfonic acid, a styrene sulfonate, a vinyl sulfonic acid, a vinyl sulfonate, and any combination of the foregoing.

[0122] In an embodiment, the acrylamide derivative is an *N*-alkyl acrylamide. In a further embodiment, the *N*-alkyl acrylamide is selected from the group consisting of: *N,N*-dimethylacrylamide, sodium 2-acrylamido-2-methylpropanesulfonate, 2-acrylamido-2-methylpropanesulfonic acid, *N*-(hydroxymethyl)acrylamide, *N*-(hydroxyethyl)acrylamide, acrylamide, and *N*-acryloyl morpholine.

[0123] In an embodiment, the vinyl pyrrolidone is 1-vinyl-2-pyrrolidone.

[0124] In an embodiment, the styrene sulfonate is an alkali metal 4-styrenesulfonate.

[0125] In an embodiment, the polymer comprises at least 25 mole% of *N*-isopropylacrylamide, *N*-propyl acrylamide, *N,N*-diethyl acrylamide; and any combination thereof.

[0126] In cases where the setting temperature is greater than a lower critical solution temperature ("LCST") of the polymer, at least some of any such dissolved polymer will precipitate to increase the resiliency of the set cement. At least in such cases, the polymer is not expected to interact with the chemistry of the setting of the hydraulic cement or the rate, and, therefore, the precipitating polymer is not expected to retard the thickening time or setting of the hydraulic cement.

[0127] In various embodiments, the polymer can be selected for having a lower critical solution temperature ("LCST") to be in the range of about 60 °F (15 °C) to about 212 °F (100 °C). In some of these embodiments, the polymer can be selected such that the LCST is at least 120 °F (49 °C) to avoid undesired precipitation of polymer during storage or shipping, for example, on a hot day at a well site.

Hydraulic Cement

[0128] While various hydraulic cements can be utilized in the cement compositions, Portland cement is generally preferred, and can be, for example, one or more of the various types identified as API Classes A-H and J cements. These cements are classified and defined in API Specification for Materials and Testing for Well Cements, API Specification 10A, 21st Edition dated Sep. 1, 1991, of the American Petroleum Institute, Washington, D.C. API Portland cements generally have a maximum particle size of about 90 microns and a specific surface (sometimes referred to as Blaine Fineness) of about 3900 square centimeters per gram. A highly useful and effective cement slurry base for use in accordance with this invention comprises API Class H Portland cement mixed with water to provide a density of from about 11.3 lb/gal to about 18.0 lb/gal of water.

Water

[0129] The term “water” is used generally herein to include fresh water or brine, unless the context otherwise requires. As used herein, the term “brine” is intended to include, unless the context otherwise requires, any aqueous solution having greater than 1,000 ppm total dissolved mineral salts.

Polymer

[0130] Polymers or certain copolymers of *N*-isopropylacrylamide, *N*-propyl acrylamide, and *N,N*-diethyl acrylamide can have the characteristic of precipitating from solution with increasing temperature.

[0131] For example, poly(*N*-isopropylacrylamide) (“PNIPAM”) and copolymers containing *N*-isopropylacrylamide (“NIPAM”) exhibit a thermoresponsive behavior in aqueous solution. NIPAM can be copolymerized, for example, with one or more other monomers to alter or adjust the thermoresponsive and solubility characteristics in aqueous solution.

[0132] PNIPAM chains have hydrophilic domains below the lower critical solution temperature (“LCST”) and hydrophobic domains above the LCST. R. Pelton, *Poly(N-*

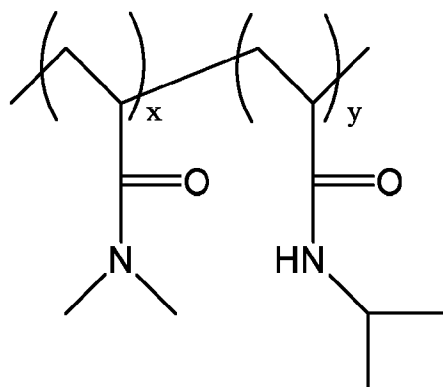
isopropylacrylamide) (PNIPAM) is never hydrophobic, J Colloid Interface Sci., 2010 Aug 15;348(2):673-4.

[0133] The NIPAM is believed to be responsible for the thermoresponsive precipitation of such a polymer. A lower critical solution temperature (LCST) describes a temperature above which hydrophobic domains are formed along the polymer chain leading to the formation of colloidal suspensions. Depending on the monomer ratio of the NIPAM/DMAC copolymer, the temperature at which the hydrophobic domains are formed can vary.

[0134] A description of the mechanism of precipitation is included in: I. C. Barker, J. M. G. Cowie, T. N. Huckerby, D. A. Shaw, I. Soutar, and L. Swanson, *Studies of the "Smart" Thermoresponsive Behavior of Copolymers of N-Isopropylacrylamide and N,N-Dimethylacrylamide in Dilute Aqueous Solution*, Macromolecules 2003, 36, 7765-7770). As described in the Abstract of this reference: "Various fluorescence techniques and cloud point measurements have been used to study the effects of altering the hydrophilic/hydrophobic balance in a series of N-isopropylacrylamide (NIPAM)/N,N-dimethylacrylamide (DMAC) statistical copolymers upon the smart thermal responses of these systems in dilute aqueous solution. As expected, incorporation of DMAC into the polymer structure raises its lower critical solution temperature to an extent dependent upon DMAC content. However, use of such a hydrophilic modifier reduces the magnitude of the collapse transition that characterizes the macromolecule's thermal response. In PNIPAM, the LCST is associated with a conformational transition between a coil and a globule. However, introduction of DMAC derivatives into the polymer expands its 'globular' form into a much more open structure that progressively loses its capacity for solubilization of organic guests. Consequently, although copolymerization with more polar monomers can be used to raise the LCST of NIPAM-based thermoresponsive polymers, the value of this approach will be limited in applications requiring switchable carrier/release properties." As the DMAC content of the polymer is increased, the LCST is raised, the transition becomes more diffuse, and its "intensity" reduces. In addition, the article discusses that cross-linking of the polymer increases the critical temperature.

[0135] This property of NIPAM/DMAC copolymers is adapted to provide a polymeric material that can be dissolved in water at a lower temperature, and then as the temperature increases the polymeric material will precipitate.

[0136] This additive can be dissolved in a liquid at the surface and, therefore, has no stability issues when included in a cement slurry and pumped downhole. Although it may be useful in some application, it is not necessary for such a NIPAM copolymer to be included in a cement slurry as an emulsion or suspension. Upon heating, the dissolved additive will precipitate to form particles that lower the Young's modulus of the set cement. An additive according to this disclosure can be tailored to precipitate solid material at varying temperatures.



Poly(N-isopropylacrylamide-co-N,N-dimethylacrylamide)

[0137] For the poly(N-isopropylacrylamide-co-N,N-dimethylacrylamide) shown above, x and y represent the numbers of the different monomeric units of the polymer, which can be the same or different. In addition, it should be understood that the polymer can be a random co-polymer or a block co-polymer.

Examples

[0138] To facilitate a better understanding of the present disclosure, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the entire scope of the disclosure.

The chart below shows a comparison of set cement properties for various SBC elastomeric particulates and the liquid-based additive of this disclosure.

[0139] A 16.4 lb/gal cement slurry was used in the examples consisting of 100% by weight of cement Texas Lehigh Class H Cement, sodium silicate (finely ground powder form) at 2% by weight of cement), the respective additive listed, and fresh water.

[0140] The elastomeric-based particulates used in some of the example cement compositions were as follows. SBC #1 is a particulate of a styrene butadiene copolymer ("SBC") (monomer ratio about 30:70), which has a specific gravity around 1. SBC #2 is a particulate of a styrene butadiene copolymer ("SBC") (monomer ratio about 20:80), which has a specific gravity around 1. SBC #1 with barite is a particulate of SBC #1 that includes a sufficient concentration of incorporated barite in the matrix of the solid SBC #1 to obtain a specific gravity of about 2. Similarly, SBC #2 with barite is a particulate of SBC #1 that includes a sufficient concentration of incorporated barite in the matrix of the solid SBC #2 to obtain a specific gravity of about 2.

[0141] A high molecular weight NIPAM/DMAC copolymer is a copolymer of N-isopropylacrylamide (NIPAM) and N,N-dimethylacrylamide ("DMAC") (about 50/50 mole percent). Without a chain transfer agent, the molecular weight of the formed polymer is very high. At standard laboratory conditions, only up to about 5% by weight of the high molecular weight NIPAM/DMAC copolymer can be dissolved in water without the solution being excessively viscous such that it is difficult to mix with a dry blend of the cementitious material. In an embodiment, the viscosity of an aqueous solution of the polymer is less than about 5,000 cP, and preferably less than about 4,000 cP, which viscosities are measured at a low shear rate of about 1 sec^{-1} and standard laboratory conditions.

[0142] A low molecular weight NIPAM/DMAC copolymer is a copolymer of N-isopropylacrylamide (NIPAM) and N,N-dimethylacrylamide (DMAC) (about 50/50 mole percent). This polymer is synthesized with a chain transfer agent to keep the molecular weight of the polymer sufficiently low to thereby allow a high concentration (that is, solubility) of the polymer in water to be achieved. At standard laboratory conditions, up to about 40% by weight of the low molecular weight NIPAM/DMAC copolymer can be dissolved in water without the

solution being excessively viscous such that it is difficult to mix with a dry blend of the cementitious material. In an embodiment, the viscosity of an aqueous solution of the polymer is less than about 5,000 cP, and preferably less than about 4,000 cP, which viscosities are measured at a low shear rate of about 1 sec⁻¹ and standard laboratory conditions.

[0143] Table 1 shows a comparison of compressive strength, Young's modulus, and Poisson's ratio between the above additives in the 16.4 lb/gal Class H Cement base cement slurry after setting.

[0144] Regarding the high molecular weight NIPAM/DMAC copolymer, the % by weight of cement shown in Table 1 is after solidification of the copolymer. Regarding the low molecular weight NIPAM/DMAC copolymer, the % by weight of cement ("% bwoc") shown in Table 1 is after solidification of the copolymer.

Table 1

Additive	Total % Solids by Weight of Cement (% bwoc)	Compressive Strength (psi)	Young's Modulus (psi)	Poisson's Ratio
SBC #1	7.5	5060	1.76E6	0.20
SBC #2	7.5	5340	1.76E6	0.19
SBC #1 with barite	15	3810	1.45E6	0.19
SBC #2 with barite	15	4340	1.46E6	0.19
high molecular weight NIPAM/DMAC copolymer (5% by weight aqueous solution)	7.5	1170	1.19E6	0.16
low molecular weight NIPAM/DMAC copolymer (40% by weight aqueous solution)	7.5	2710	1.26E6	0.18

[0145] The pump time charts are shown in Figure 1 and Figure 2, the control has no additive and the low molecular weight NIPAM/DMAC copolymer test has an equivalent of 7.5 % by weight of cement of the active polymer.

[0146] In addition, thickening time tests were performed on a control cement compositions without any NIPAM polymer and on another cement composition including a NIPAM polymer according to the disclosure.

[0147] **Figure 1** shows the consistency of a cement slurry as a control, without low molecular weight NIPAM/DMAC copolymer (NIPAM/DMAC copolymer 40% active aqueous solution). This control composition reached 40 Bc at about 46 minutes, 50 Bc at about 51 minutes, 70 Bc at about 58 minutes, and 100 Bc at about 1 hour and 5 minutes.

[0148] **Figure 2** shows the consistency of a cement slurry comprising 1.82 gal/sack (7.5 eq. %bwoc) low molecular weight NIPAM/DMAC copolymer (NIPAM/DMAC copolymer 40% active aqueous solution). This composition reached 40 Bc at 42 minutes, 50 Bc at about 50 minutes, 70 Bc at about 57 minutes, and 100 Bc at about 1 hour and 7 minutes.

[0149] These thickening time tests of **Figure 1** and **Figure 2** show that there were no significant retarding effects by the polymer on the set time of the cement. Essentially, it is inert to the thickening time and setting of the cement slurry.

Method of Cementing in a Well

[0150] According to an embodiment of the disclosure, a method of cementing in a well is provided, the method including the steps of: forming a hydraulic cement composition according to the disclosure; and introducing the composition into the well.

[0151] According to a further embodiment, the design temperature of the treatment zone in the well is greater than a LCST of the polymer.

Forming Fluid

[0152] A fluid such as a hydraulic cement composition according to this disclosure can be prepared at the job site, prepared at a plant or facility prior to use, or certain components of the fluid can be pre-mixed prior to use and then transported to the job site. Certain components of the fluid may be provided as a “dry mix” to be combined with fluid or other components prior to or during introducing the fluid into the well.

[0153] In certain embodiments, the preparation of a fluid can be done at the job site in a method characterized as being performed “on the fly.” The term “on-the-fly” is used herein to include methods of combining two or more components wherein a flowing stream of one element is continuously introduced into flowing stream of another component so that the streams are combined and mixed while continuing to flow as a single stream as part of the on-going treatment. Such mixing can also be described as “real-time” mixing.

Introducing Into Well or Treatment Zone

[0154] Often the step of delivering a fluid into a well or treatment zone of a well is within a relatively short period after forming the fluid, for example, less within 30 minutes to one hour. More preferably, the step of delivering the fluid is immediately after the step of forming the fluid, which is “on the fly.”

[0155] It should be understood that the step of delivering a fluid into a well can advantageously include the use of one or more fluid pumps.

Allowing Time for Setting in the Well

[0156] After the step of introducing a cementing composition according to the disclosure, time should be allowed for the setting of the composition in place in the well, unless it was not properly placed and needs to be cleaned out before setting. This preferably occurs with time under the conditions in the zone of the subterranean fluid.

Flow Back Conditions

[0157] In an embodiment, a step of flowing back from the well is after at least sufficient time for setting of the cement composition in the well.

Producing Hydrocarbon from Subterranean Formation

[0158] After such use of a cement composition according to the disclosure, a step of producing hydrocarbon from the well or a particular zone is often a desirable objective. In some applications, however, an objective may be plugging a wellbore or sealing a zone.

Conclusion

[0159] Therefore, the present disclosure is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein.

[0160] The exemplary hydraulic cement compositions disclosed herein may directly or indirectly affect one or more components or pieces of equipment associated with the preparation, delivery, recapture, recycling, reuse, or disposal of the disclosed hydraulic cement compositions. For example, the disclosed hydraulic cement compositions may directly or indirectly affect one or more mixers, related mixing equipment, mud pits, storage facilities or units, fluid separators, heat exchangers, sensors, gauges, pumps, compressors, and the like used generate, store, monitor, regulate, or recondition the exemplary hydraulic cement compositions. The disclosed hydraulic cement compositions may also directly or indirectly affect any transport or delivery equipment used to convey the hydraulic cement compositions to a well site or downhole such as, for example, any transport vessels, conduits, pipelines, trucks, tubulars, or pipes used to fluidically move the hydraulic cement compositions from one location to another, any pumps, compressors, or motors (for example, topside or downhole) used to drive the hydraulic cement compositions into motion, any valves or related joints used to regulate the pressure or flow rate of the hydraulic cement compositions, and any sensors (*i.e.*, pressure and temperature), gauges, or combinations thereof, and the like. The disclosed hydraulic cement compositions may also directly or indirectly affect the various downhole equipment and tools that may come into contact with the chemicals/fluids such as, but not limited to, drill string, coiled tubing, drill pipe, drill collars, mud motors, downhole motors or pumps, floats, MWD/LWD tools and related telemetry equipment, drill bits (including roller cone, PDC, natural diamond, hole openers, reamers, and coring bits), sensors or distributed sensors, downhole heat exchangers, valves and corresponding actuation devices, tool seals, packers and other wellbore isolation devices or components, and the like.

[0161] The particular embodiments disclosed above are illustrative only, as the present disclosure may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. It is, therefore, evident that the

particular illustrative embodiments disclosed above may be altered or modified and all such variations are considered within the scope of the present disclosure.

[0162] The various elements or steps according to the disclosed elements or steps can be combined advantageously or practiced together in various combinations or sub-combinations of elements or sequences of steps to increase the efficiency and benefits that can be obtained from the disclosure.

[0163] It will be appreciated that one or more of the above embodiments may be combined with one or more of the other embodiments, unless explicitly stated otherwise.

[0164] The illustrative disclosure can be practiced in the absence of any element or step that is not specifically disclosed or claimed.

[0165] Furthermore, no limitations are intended to the details of construction, composition, design, or steps herein shown, other than as described in the claims.

What is claimed is:

1. A hydraulic cement composition comprising:
 - (A) a hydraulic cement;
 - (B) at least a sufficient concentration of water to form a pumpable slurry with the hydraulic cement; and
 - (C) a polymer selected from the group consisting of:
 - (i) a homopolymer of one monomer selected from the group consisting of: *N*-isopropylacrylamide, *N*-propyl acrylamide, and *N,N*-diethyl acrylamide;
 - (ii) a copolymer consisting of two or more monomers selected from the group consisting of: *N*-isopropylacrylamide, *N*-propyl acrylamide, and *N,N*-diethyl acrylamide; and
 - (iii) a copolymer comprising:
 - (a) one or more first monomers selected from the group consisting of: *N*-isopropylacrylamide, *N*-propyl acrylamide, *N,N*-diethyl acrylamide, and any combination thereof; and
 - (b) one or more second monomers selected from the group consisting of: acrylamide, an acrylamide derivative other than one of the first monomers, methacrylamide, an *N*-alkyl methacrylamide, *N*-methyl-*N*-vinylacetamide, *N*-vinylformamide, a vinyl pyrrolidone, a vinyl pyridine, *N*-vinylcaprolactam, *N*-methyl-*N*-vinylacetamide, a styrene sulfonic acid, a styrene sulfonate, a vinyl sulfonic acid, a vinyl sulfonate, and any combination of the foregoing.
2. The hydraulic cement composition according to claim 1, wherein: the acrylamide derivative is selected from the group consisting of an *N*-alkyl acrylamide.
3. The hydraulic cement composition according to claim 2, wherein the *N*-alkyl acrylamide is selected from the group consisting of: *N,N*-dimethylacrylamide, sodium 2-acrylamido-2-methylpropanesulfonate, 2-acrylamido-2-methylpropanesulfonic acid, *N*-(hydroxymethyl)acrylamide, *N*-(hydroxyethyl)acrylamide, acrylamide, and *N*-acryloyl morpholine.

4. The hydraulic cement composition according to claim 1, wherein the vinyl pyrrolidone is 1-vinyl-2-pyrrolidone.

5. The hydraulic cement composition according to claim 1, wherein the styrene sulfonate is an alkali metal 4-styrenesulfonate.

6. The hydraulic cement composition according to claim 1, wherein the polymer comprises at least 25 mole% of *N*-isopropylacrylamide, *N*-propyl acrylamide, *N,N*-diethyl acrylamide; and any combination thereof.

7. The hydraulic cement composition according to claim 1, wherein the polymer is not crosslinked.

8. The hydraulic cement composition according to claim 1, wherein the polymer has a sufficiently low molecular weight such that the polymer is at least 5% by weight soluble in water and an aqueous solution of the polymer at that concentration is less than about 5,000 cP.

9. The hydraulic cement composition according to claim 1, wherein the polymer has a sufficiently low molecular weight such that the polymer is at least 40% by weight soluble in water and an aqueous solution of the polymer at that concentration is less than about 5,000 cP.

10. The hydraulic cement composition according to claim 1, additionally comprising a set retarder.

11. A method of cementing in a well, the method comprising:
forming a hydraulic cement composition comprising:
- (A) a hydraulic cement;
 - (B) at least a sufficient concentration of water to form a pumpable slurry with the hydraulic cement; and
 - (C) a polymer selected from the group consisting of:
 - (i) a homopolymer of one monomer selected from the group consisting of: *N*-isopropylacrylamide, *N*-propyl acrylamide, and *N,N*-diethyl acrylamide;
 - (ii) a copolymer consisting of two or more monomers selected from the group consisting of: *N*-isopropylacrylamide, *N*-propyl acrylamide, and *N,N*-diethyl acrylamide; and
 - (iii) a copolymer comprising:
 - (a) one or more first monomers selected from the group consisting of: *N*-isopropylacrylamide, *N*-propyl acrylamide, *N,N*-diethyl acrylamide, and any combination thereof; and
 - (b) one or more second monomers selected from the group consisting of: acrylamide, an acrylamide derivative other than one of the first monomers, methacrylamide, an *N*-alkyl methacrylamide, *N*-methyl-*N*-vinylacetamide, *N*-vinylformamide, a vinyl pyrrolidone, a vinyl pyridine, *N*-vinylcaprolactam, *N*-methyl-*N*-vinylacetamide, a styrene sulfonic acid, a styrene sulfonate, a vinyl sulfonic acid, a vinyl sulfonate, and any combination of the foregoing; and
- introducing the hydraulic cement composition into a treatment zone of the well.
12. The method according to claim 11, wherein: the acrylamide derivative is selected from the group consisting of an *N*-alkyl acrylamide.

13. The method according to claim 12, wherein the *N*-alkyl acrylamide is selected from the group consisting of: *N,N*-dimethylacrylamide, sodium 2-acrylamido-2-methylpropanesulfonate, 2-acrylamido-2-methylpropanesulfonic acid, *N*-(hydroxymethyl)acrylamide, *N*-(hydroxyethyl)acrylamide, acrylamide, and *N*-acryloyl morpholine.

14. The method according to claim 11, wherein the vinyl pyrrolidone is 1-vinyl-2-pyrrolidone.

15. The method according to claim 11, wherein the styrene sulfonate is an alkali metal 4-styrenesulfonate.

16. The method according to claim 11, wherein the polymer comprises at least 25 mole% of *N*-isopropylacrylamide, *N*-propyl acrylamide, *N,N*-diethyl acrylamide; and any combination thereof.

17. The method according to claim 11, wherein the polymer is not crosslinked.

18. The method according to claim 11, wherein the polymer has a sufficiently low molecular weight such that the polymer is at least 5% by weight soluble in water and an aqueous solution of the polymer at that concentration is less than about 5,000 cP.

19. The method according to claim 11, wherein the polymer has a sufficiently low molecular weight such that the polymer is at least 40% by weight soluble in water and an aqueous solution of the polymer at that concentration is less than about 5,000 cP.

20. The method according to claim 11, additionally comprising a set retarder.

21. The method according to claim 11, wherein the design temperature of the treatment zone in the well is greater than a LCST of the polymer.

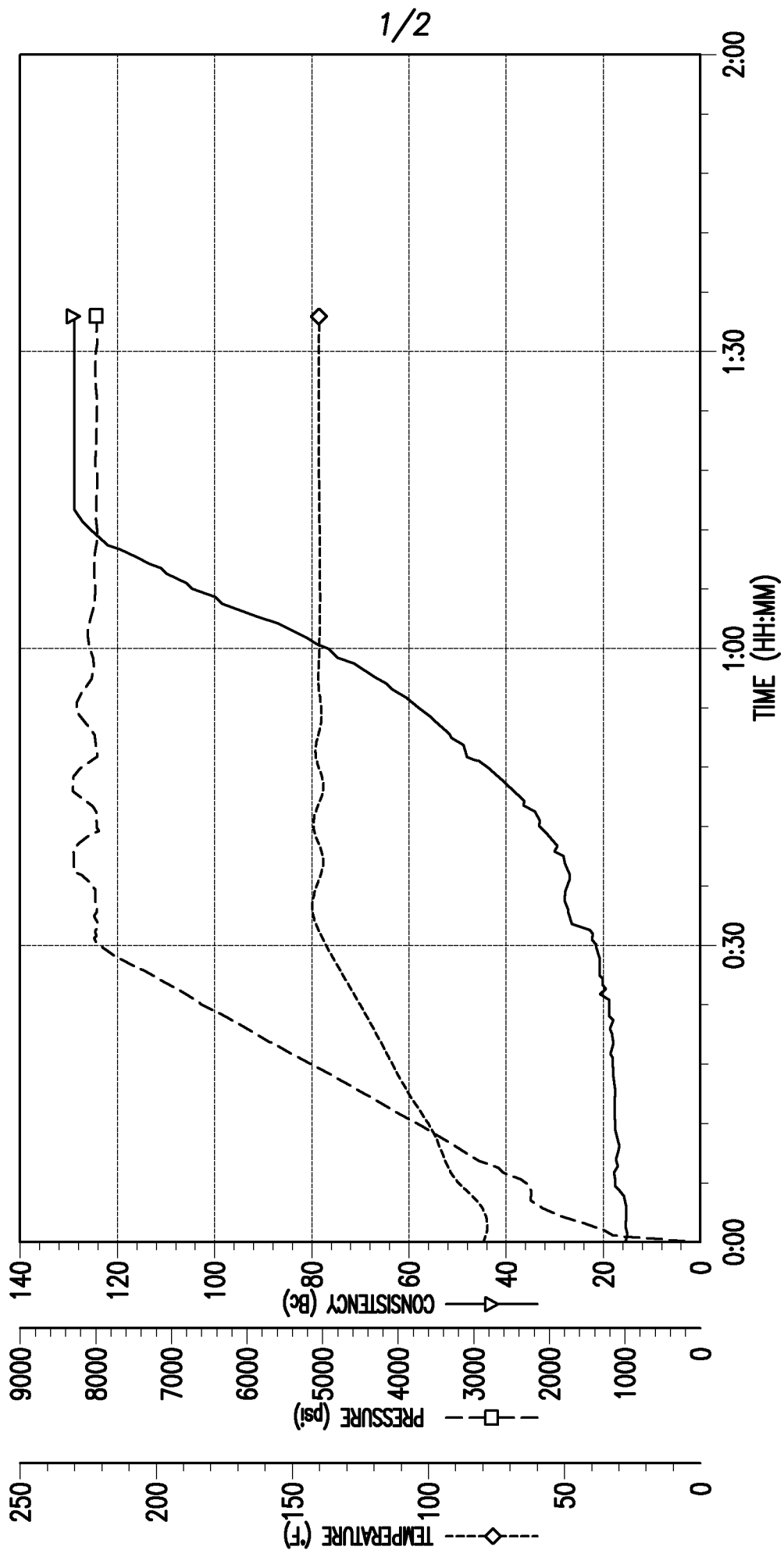


FIG. 1

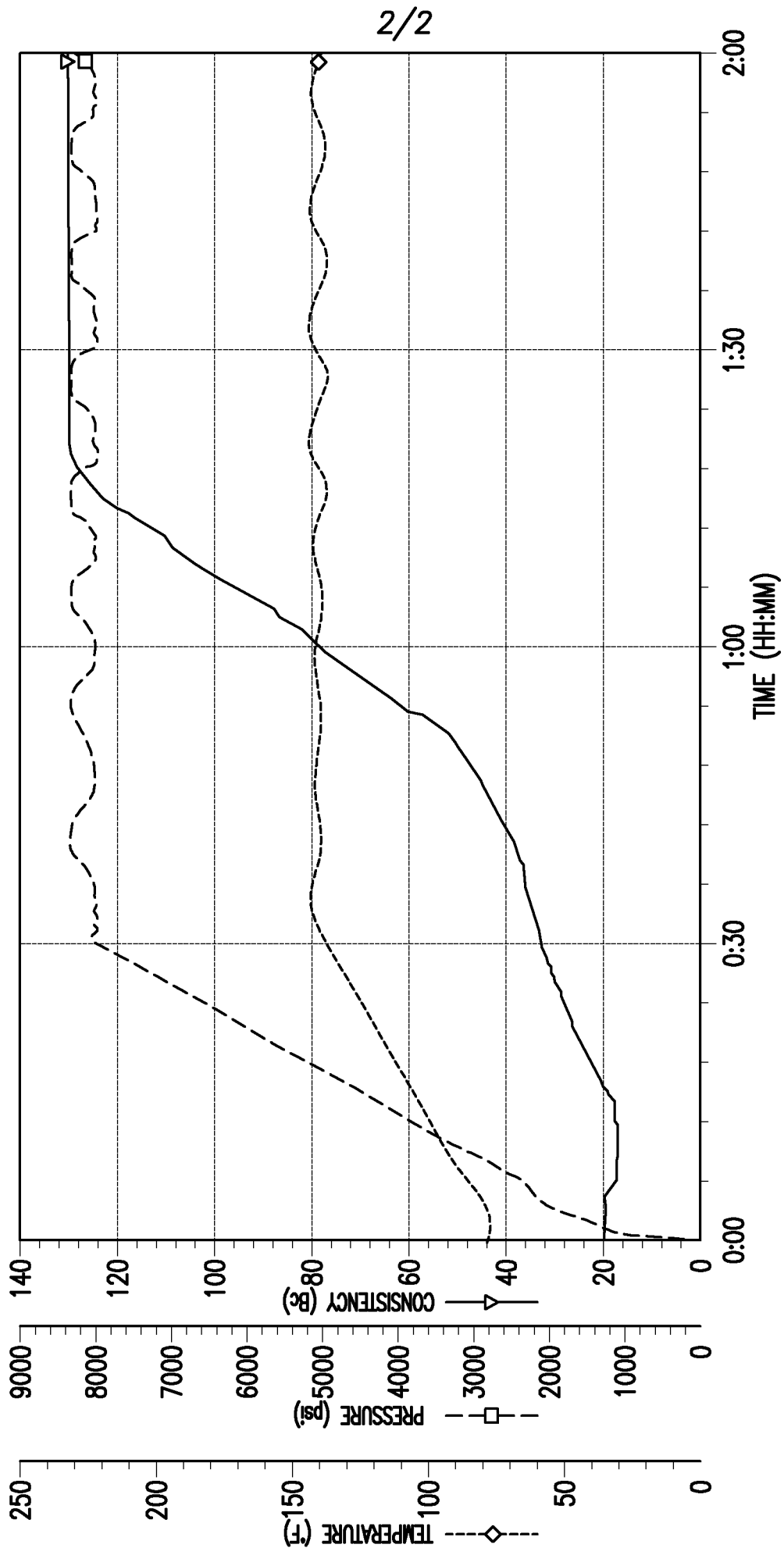


FIG. 2