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(54) **Title:** HIGH TEMPERATURE AND HIGH PRESSURE CEMENT RETARDER COMPOSITION AND USE THEREOF

(57) **Abstract:** Water soluble or water dispersible compositions comprising a copolymer may be used for the servicing of subterranean wells. The copolymer comprises an allyloxy linkage and its functional derivatives. The copolymer may be used to retard cement slurries designed for placement in high pressure, high temperature wells. The cement slurries are prepared with a hydraulic cement.



HIGH TEMPERATURE AND HIGH PRESSURE CEMENT RETARDER COMPOSITION AND USE THEREOF

CROSS-REFERENCE TO RELATES APPLICATION(S)

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 62/193,847 filed July 17, 2015 entitled "High Temperature and High Pressure Cement Retarder Composition and Use Thereof" to Melbouci et al. and U.S. Provisional Application Serial No. 62/269,267 filed December 18, 2015 entitled "High Temperature and High Pressure Cement Retarder Composition and Use Thereof" to Caritey et al, the disclosure of each of the provisional applications is incorporated by reference herein in its entirety.

FIELD OF THE DISCLOSURE

[0002] The presently disclosed and/or claimed process(es), procedure(s), method(s), product(s), result(s), and/or concept(s) (collectively referred to hereinafter as the "presently disclosed and/or claimed concept(s)") relates generally to a water soluble or water dispersible composition comprising a copolymer and use in subterranean wells. More particularly, but not by way of limitation, the presently disclosed and/or claimed concept(s) relates to a copolymer comprising an allyloxy linkage and its functional derivatives, and its use in subterranean wells; for example, as a high pressure/high temperature (HPHT) cement retarder composition.

BACKGROUND

[0003] Polymers are used extensively in well completion, well stimulation and enhanced oil-recovery processes. Synthetic, organic, and inorganic polymers, cellulose ethers, guar gum and guar derivatives, and other biopolymers such as xanthan gum, diutan gum and welan gum are widely used in the gas/oil field applications. These polymers are also applied in a variety of formation-damage control applications and as dispersing agents.

[0004] Well completion refers to operations performed during the period between the commencement of drilling and the time at which the well is put into production. These operations may include additional drilling-in, placement of downhole hardware, perforating, gravel packing and removing downhole debris. A completion fluid is often defined as a wellbore fluid used to facilitate such operations. The completion fluid's primary function is to control the

pressure of the formation fluid by virtue of its specific gravity. The type of operation performed, the bottomhole conditions, and the nature of the formation will dictate other properties such as viscosity. Completion fluids are also used clean out the drilled borehole. Oil well cement compositions are used during completion operation to make a permanent, leak proof well for continuous use.

[0005] During construction of oil and gas wells, a rotary drill is typically used to bore through subterranean formations of the earth to form a borehole. As the rotary drill bores through the earth, a drilling fluid, also known in the industry as a "mud" or "drilling fluid," is circulated within the borehole. Drilling fluids are usually pumped from the surface through the interior of the drill pipe. By continuously pumping the drilling fluids through the drill pipe, the drilling fluids can be circulated out the bottom of the drill pipe and back up to the well surface through the annular space between the wall of the wellbore and the drill pipe. The hydrostatic pressure created by the column of mud in the hole prevents blowouts that might otherwise occur due to the high pressures encountered within the well. The drilling fluid is also used to help lubricate and cool the drill bit, and facilitates the removal of cuttings as the borehole is drilled.

[0006] Once the wellbore has been drilled, a casing string is lowered into the wellbore. A cement slurry is then pumped down the casing interior. The cement slurry exits the casing interior at the bottom the casing string and travels upward to fill the annular space between the exterior of the casing and the borehole wall. Alternatively, a "reverse cementing" technique may be applied wherein the cement slurry is pumped down the annulus from the surface. The cement slurry is then allowed to set and harden in the annulus, thereby forming a cement sheath.

[0007] A primary function of the cement sheath is to restrict fluid movement between subterranean formations and to support the casing. In addition, the cement sheath may protect the casing from corrosion, prevent sloughing or erosion of the wellbore, prevent blowouts by quickly sealing formations, protect the casing from shock loads when drilling deeper into the well or seal lost-circulation or thief zones. Additionally, cements may be used in remedial operations such as squeeze cementing and plug cementing.

[0008] In most cases, cement slurries for use in such applications contain hydraulic cements that set and develop compressive strength due to a hydration reaction, and thus can be set under water. For well cementing, hydraulic cement is mixed with sufficient water to form a pumpable

cement slurry. Examples of hydraulic cements include portland cement, calcium aluminate cement, lime-silica blends and certain fly ashes and blast furnace slags.

[0009] During primary cementing, when the cement slurry is placed in the annulus between a casing or liner and the adjacent earth formations, fluid-loss control is of concern. Fluid loss is the escape of the aqueous phase from a cement slurry, resulting from a filtration process as the slurry is pumped past permeable formations. Loss of a significant amount of water from the cement slurry may detrimentally affect the slurry's rheological properties, the ability to place the slurry in the well successfully, and the ultimate integrity of the cement sheath. During remedial cementing operations, fluid-loss control is necessary to achieve the precise cement slurry placement associated with such operations.

[0010] Deep gas and oil wells may have temperature gradients that may range from near freezing at the surface (e.g., deepwater) to 260°C or even above (i.e. 315°C as described below in paragraph [0046]) at the bottom. Primary cementing of the deep, hot sections can be very challenging. The pumping times necessary to place the cement slurry may be several hours, and high temperatures accelerate the cement hydration reactions. The required pumping times at high temperatures are achieved by incorporating additives that slow down or delay the hydration reactions. Such additives are called "retarders." A wide variety of retarders has been developed by the cementing industry. Some of the more common ones include lignosulfonates, gluconates, glucoheptonates and organophosphonates. Some basic organic polymers or copolymers as described paragraph [0028] below based on acrylic derivatives monomers (sulfonated and or carboxylated) including also amides derivatives are also used. Boric acid or borax may be further added to intensify or extend the retarders' ability to control cement hydration.

[0011] Further information concerning the cementing process and cement retarders may be found in the following publications.

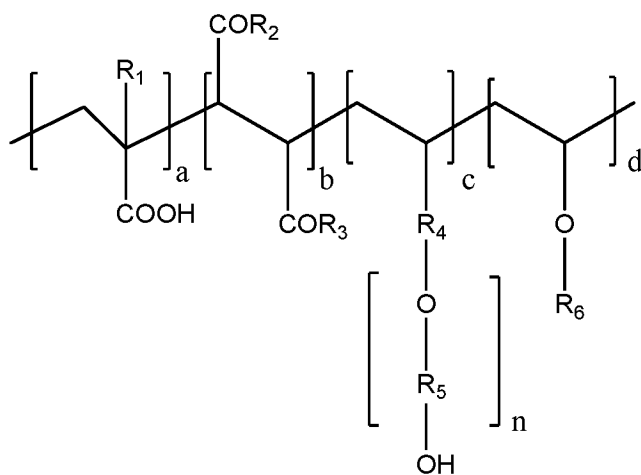
[0012] Nelson EB: "Well Cementing Fundamentals," *Oilfield Review* **24**, no. 2 (Summer 2012): 59–60.

[0013] Nelson EB, Michaux M and Drochon B: "Cement Additives and Mechanisms of Action," in Nelson EB and Guillot D (eds.): *Well Cementing—2nd Edition*, Houston: Schlumberger (2006): 54–58.

SUMMARY

[0014] This summary is provided to introduce a selection of concepts that are further described below in the detailed description. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used as an aid in limiting the scope of the claimed subject matter.

[0015] In an aspect, embodiments relate to compositions comprising a copolymer represented by Formula (I):



Formula (I)

wherein:

R₁ is hydrogen, or straight or branched C₁-C₅ alkyl;

R₂ and R₃ are independently OH or NH₂;

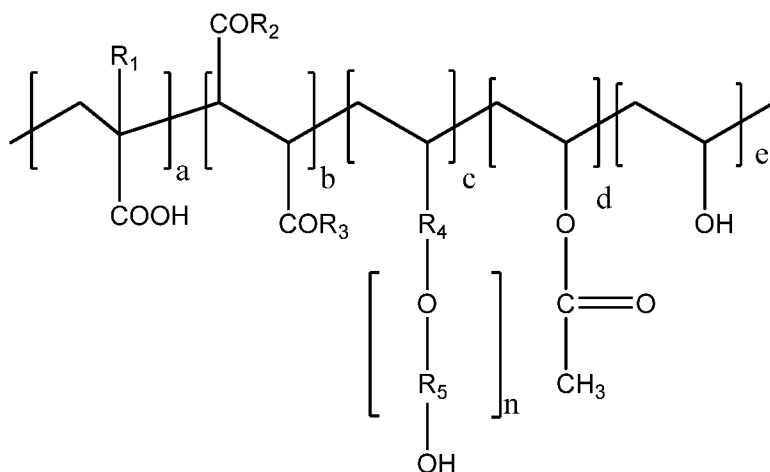
R₄ is C=O, or independently straight or branched C₁-C₅ alkyl;

R₅ is independently straight or branched C₁-C₅ alkyl;

R₆ is hydrogen or COR₇, wherein R₇ is straight or branched C₁-C₅ alkyl; and

n is an integer from 1 to 100.

[0016] In a further aspect, embodiments relate to compositions comprising a copolymer represented by Formula (VI):



Formula (VI)

wherein:

R₁ is hydrogen, or straight or branched C₁-C₅ alkyl;

R₂ and R₃ are independently OH or NH₂;

R₄ is C=O or independently straight or branched C₁-C₅ alkyl;

R₅ is independently straight or branched C₁-C₅ alkyl; and

n is an integer from 1 to 100.

[0017] In yet a further aspect, embodiments relate to compositions comprising water, a hydraulic cement and a retarder comprising the copolymer represented by Formula (I) or Formula (VI) or both.

[0018] In yet a further aspect, embodiments relate to methods for cementing a subterranean well having a wellbore. A composition is provided that comprises water, a hydraulic cement and a retarder comprising the copolymer represented by Formula (I) or Formula (VI) or both. The composition is then placed in the wellbore.

[0019] In yet a further aspect, embodiments relate to methods for treating a subterranean well having a wellbore. A composition is provided that comprises water, a hydraulic cement and a retarder comprising the copolymer represented by Formula (I) or Formula (VI) or both. The composition is then placed in the wellbore.

DETAILED DESCRIPTION

[0020] At the outset, it should be noted that in the development of any such actual embodiment, numerous implementation—specific decisions are 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 disclosure 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. The term about should be understood as any amount or range within 10% of the recited amount or range (for example, a range from about 1 to about 10 encompasses a range from 0.9 to 11). Also, in the summary 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 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 possible number along the continuum between about 1 and about 10. Furthermore, one or more of the data points in the present examples may be combined together, or may be combined with one of the data points in the specification to create a range, and thus include each possible value or number within this range. Thus, even if specific data points within the range, or even no data points within the range, are explicitly identified or refer to a few specific, it is to be understood that inventors appreciate and understand that any data points within the range are to be considered to have been specified, and that inventors possessed knowledge of the entire range and the points within the range.

[0021] Before explaining at least one embodiment of the presently disclosed and/or claimed concept(s) in detail, it is to be understood that the presently disclosed and/or claimed concept(s) is not limited in its application to the details of construction and the arrangement of the components or steps or methodologies set forth in the following description or illustrated in the drawings. The presently disclosed and/or claimed concept(s) is capable of other embodiments or of being practiced or carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein is for the purpose of description and should not be regarded as limiting.

[0022] Unless otherwise defined herein, technical terms used in connection with the presently disclosed and/or claimed concept(s) shall have the meanings that are commonly understood by those of ordinary skill in the art. Further, unless otherwise required by context, singular terms shall include pluralities and plural terms shall include the singular.

[0023] All patents, published patent applications, and non-patent publications mentioned in the specification are indicative of the level of skill of those skilled in the art to which the presently disclosed and/or claimed concept(s) pertains. All patents, published patent applications, and non-patent publications referenced in any portion of this application are herein expressly incorporated by reference in their entirety to the same extent as if each individual patent or publication was specifically and individually indicated to be incorporated by reference.

[0024] All of the articles and/or methods disclosed herein can be made and executed without undue experimentation in light of the present disclosure. While the articles and methods of the presently disclosed and/or claimed concept(s) have been described in terms of preferred embodiments, it will be apparent to those of ordinary skill in the art that variations may be applied to the articles and/or methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the presently disclosed and/or claimed concept(s). All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the presently disclosed and/or claimed concept(s).

[0025] As utilized in accordance with the present disclosure, the following terms, unless otherwise indicated, shall be understood to have the following meanings.

[0026] The use of the word “a” or “an” when used in conjunction with the term “comprising” may mean “one,” but it is also consistent with the meaning of “one or more,” “at least one,” and “one or more than one.” The use of the term “or” is used to mean “and/or” unless explicitly indicated to refer to alternatives only if the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and “and/or.” Throughout this application, the term “about” is used to indicate that a value includes the inherent variation of error for the quantifying device, the method being employed to determine the value, or the variation that exists among the study subjects. For example, but not by way of limitation, when the term “about” is utilized, the designated value may vary by plus or minus

twelve percent, or eleven percent, or ten percent, or nine percent, or eight percent, or seven percent, or six percent, or five percent, or four percent, or three percent, or two percent, or one percent. The use of the term “at least one” will be understood to include one as well as any quantity more than one, including but not limited to, 1, 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 100, etc. The term “at least one” may extend up to 100 or 1000 or more depending on the term to which it is attached. In addition, the quantities of 100/1000 are not to be considered limiting as lower or higher limits may also produce satisfactory results. In addition, the use of the term “at least one of X, Y, and Z” will be understood to include X alone, Y alone, and Z alone, as well as any combination of X, Y, and Z. The use of ordinal number terminology (i.e., “first”, “second”, “third”, “fourth”, etc.) is solely for the purpose of differentiating between two or more items and, unless explicitly stated otherwise, is not meant to imply any sequence or order or importance to one item over another or any order of addition.

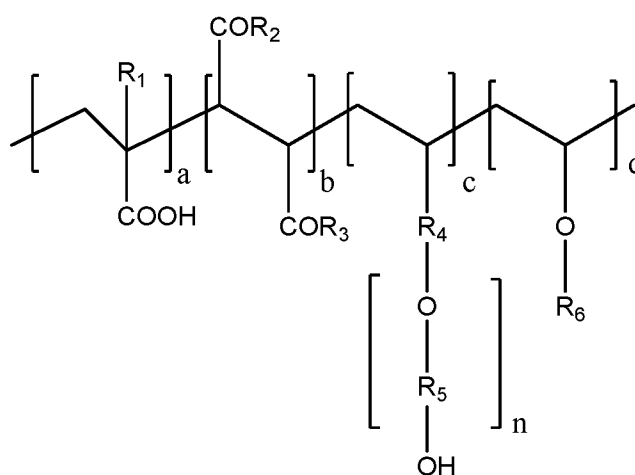
[0027] As used herein, the words “comprising” (and any form of comprising, such as “comprise” and “comprises”), “having” (and any form of having, such as “have” and “has”), “including” (and any form of including, such as “includes” and “include”) or “containing” (and any form of containing, such as “contains” and “contain”) are inclusive or open-ended and do not exclude additional, unrecited elements or method steps. The term “or combinations thereof” as used herein refers to all permutations and combinations of the listed items preceding the term. For example, “A, B, C, or combinations thereof” is intended to include at least one of: A, B, C, AB, AC, BC, or ABC and, if order is important in a particular context, also BA, CA, CB, CBA, BCA, ACB, BAC, or CAB. Continuing with this example, expressly included are combinations that contain repeats of one or more item or term, such as BB, AAA, AAB, BBC, AAABCCCC, CBBAAA, CABABB, and so forth. The skilled artisan will understand that typically there is no limit on the number of items or terms in any combination, unless otherwise apparent from the context.

[0028] As used herein any reference to “one embodiment” or “an embodiment” means that a particular element, feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment. The appearance of the phrase “in one embodiment” in various places in the specification are not necessarily all referring to the same embodiment.

[0029] The term “copolymer” as used herein will be understood to encompass a polymer produced from two or more different types of monomers. As such, the term “copolymer” may refer to a polymer produced from two different types of monomers, or a polymer produced from three different types of monomers, and/or a polymer produced from four or more different types of monomers.

[0030] The presently disclosed and/or claimed concept(s) encompasses a water soluble or dispersible composition comprising a copolymer and use of the composition in subterranean wells. More particularly, but not by way of limitation, the presently disclosed and/or claimed concept(s) relates to a copolymer containing an allyloxy linkage and its functional derivatives for use as high temperature cement retarders.

[0031] In an aspect, embodiments relate to water soluble or dispersible compositions of the presently disclosed and/or claimed concept(s) comprising a copolymer represented by Formula (I):

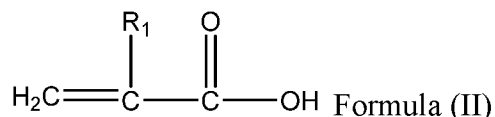


Formula (I)

where R_1 is hydrogen, or straight or branched C_1 - C_5 alkyl; R_2 and R_3 are independently OH or NH_2 ; R_4 is $C=O$, or independently straight or branched C_1 - C_5 alkyl; R_5 is independently straight or branched C_1 - C_5 alkyl; R_6 is hydrogen or COR_7 , wherein R_7 is straight or branched C_1 - C_5 alkyl; and n is an integer from 1 to about 100.

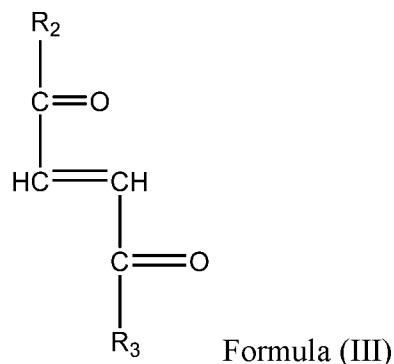
[0032] In one non-limiting embodiment, the copolymer represented by Formula (I) can be obtained by copolymerizing:

(a) 15 to 75 moles of an alpha, beta ethylenically unsaturated carboxylic acid represented by Formula (II):



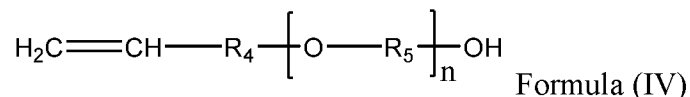
where R₁ is as defined above;

(b) 15 to 75 moles of an unsaturated dicarboxylic acid, or an unsaturated dicarboxylic amide represented by Formula (III):



where R₂ and R₃ are as defined above;

(c) 5 to 50 moles of hydroxypolyethoxyl allyl ether (PEGAE) represented by Formula (IV):



where R₄, R₅ and n are as defined above; and

(d) 5 to 50 moles of vinyl alcohol or vinyl acetate represented by Formula (V):

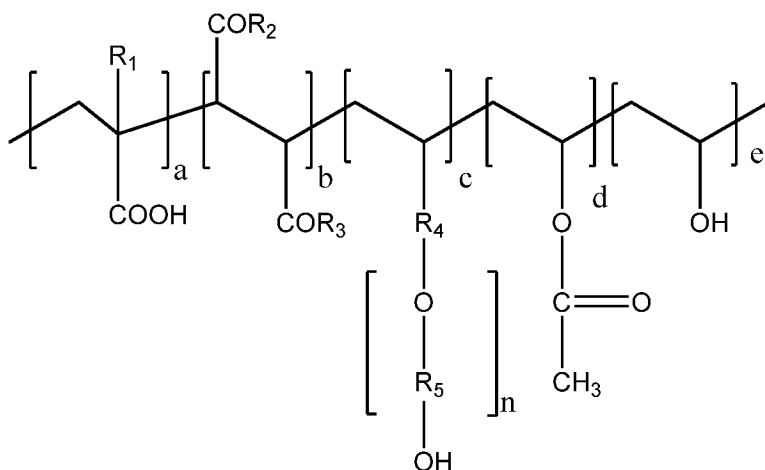


where R₆ is as defined above.

[0033] In one non-limiting embodiment, the alpha, beta ethylenically unsaturated carboxylic acid can be acrylic acid. In another non-limiting embodiment, the alpha, beta ethylenically unsaturated carboxylic acid can be an (alkyl)acrylic acid such as methacrylic acid.

[0034] The unsaturated dicarboxylic acid can include, but are not limited to, maleic acid, fumaric acid, and combinations thereof. For hydroxypolyethoxyl allyl ether (PEGAE), n can be in a range of from 1 to about 100, or from about 5 to about 50, or from about 5 to about 20, or from about 8 to about 20. In one non-limiting embodiment, n can be equal to 10.

[0035] In a further aspect, a water soluble or dispersible composition of the presently disclosed and/or claimed concept(s) comprises a copolymer represented by Formula (VI):



Formula (VI)

where R_1 - R_5 and n are as defined above.

[0036] In one non-limiting embodiment, the copolymer represented by Formula (VI) can be obtained by copolymerizing:

- (a) 15 to 75 moles of an alpha, beta ethylenically unsaturated carboxylic acid represented by Formula (II);
- (b) 15 to 75 moles of an unsaturated dicarboxylic acid, or an unsaturated dicarboxylic amide represented by Formula (III);
- (c) 5 to 50 moles of hydroxypolyethoxyl allyl ether (PEGAE) represented by Formula (IV);
- (d) 5 to 50 moles of vinyl acetate represented by Formula (V); and
- (e) 5 to 50 moles of vinyl alcohol.

[0037] The copolymers of the presently disclosed and/or claimed concept(s) may be produced by solution, emulsion, micelle or dispersion polymerization techniques. Conventional polymerization initiators such as persulfates, peroxides, and azo type initiators may be used. In the case of solution polymerization using water as a solvent, a persulfate including sodium persulfate, potassium persulfate, ammonium persulfate or the like; hydrogen peroxide or a water soluble azo initiator may be used. Further, in the case of solution polymerization an organic solvent such as a lower alcohol including methanol, ethanol, isopropanol or the like; an aliphatic hydrocarbon including n-hexane, 2-ethyl hexane, cyclohexane or the like; an aromatic hydrocarbon including toluene and xylene; and acetone, methyl ethyl ketone, ethyl acetate or the like can be used. In the case of bulk polymerization, an organic peroxide such as benzoyl

peroxide, di-t-butyl peroxide, t-butyl peroxy isobutyrate or the like; or an azo compound such as azobisisobutyronitrile may be used. Polymerization may also be initiated by radiation or ultraviolet mechanisms.

[0038] Chain transfer agents such as thioglycol acid, isopropanol, allyl alcohol, hypophosphites, amines or mercapto compounds such as mercapto ethanol may be used to regulate the molecular weight of the copolymer. Branching agents, such as methylene bisacrylamide and polyethylene glycol diacrylate, and other multifunctional crosslinking agents may further be added. The resulting copolymer may be isolated by precipitation or other well-known techniques. The polymer can be used as a solid. If polymerization is in an aqueous solution, the copolymer may simply be used in the aqueous solution form.

[0039] The weight average molecular weight of the copolymer may be varied from about 1,000 to about 1,000,000 Daltons, or from about 1,500 to about 500,000 Daltons, or from about 2,000 to about 250,000 Daltons, or from about 5,000 to about 150,000 Daltons, or from about 10,000 to about 50,000 Daltons.

[0040] The polymerization may be conducted under nitrogen purge at temperatures from about 40 °C to about 150 °C, or from about 60 °C to about 100 °C, or from about 60 °C to about 80 °C.

[0041] The initiator may be used in a proportion of from about 0.05 to about 20 wt %, or from about 0.01 to about 10 wt %, or from about 0.1 to about 2 wt %, based on the total weight of the sum of the monomers. The initiator may be added to the reaction vessel in various ways during the polymerization. It may all be placed in the reaction vessel or during the polymerization reaction, continuously or stepwise, as it is consumed.

[0042] In yet a further aspect, embodiments relate to compositions that comprise water, a hydraulic cement and a retarder comprising the copolymer of Formula (I) or the copolymer of Formula (VI) or both.

[0043] The weight average molecular weight of the copolymer may be varied from about 1,000 to about 1,000,000 Daltons, or from about 1,500 to about 500,000 Daltons, or from about 2,000 to about 250,000 Daltons, or from about 5,000 to about 150,000 Daltons, or from about 10,000 to about 50,000 Daltons.

[0044] The copolymer may be polymerized from an alpha, beta ethylenically unsaturated carboxylic acid, an unsaturated dicarboxylic acid, hydroxypolyethoxyl allyl ether, and vinyl acetate. The unsaturated dicarboxylic acid may be maleic acid or maleic anhydride.

[0045] In one non-limiting embodiment, the alpha, beta ethylenically unsaturated carboxylic acid may be acrylic acid. In another non-limiting embodiment, the alpha, beta ethylenically unsaturated carboxylic acid may be an (alkyl)acrylic acid such as methacrylic acid.

[0046] The unsaturated dicarboxylic acid can include, but are not limited to, maleic acid, maleic anhydride, fumaric acid, and combinations thereof.

[0047] The cement retarder composition is capable of delaying the set time of the cement slurry until the slurry is placed into its desired location. When used, the set time of the aqueous cement slurry may be delayed during placement at downhole temperatures as high as 315°C. Then, the cement slurry may be hardened to a solid mass at elevated temperatures within the wellbore. Further, the cement slurries used in the presently disclosed and/or claimed concept(s) may exhibit set times at elevated temperatures and pressures even in the absence of a boron based intensifier such as boric acid, borax or boroethanolamine. Other retarder intensifiers may include colloidal silica.

[0048] The hydraulic cement may comprise portland cement (e.g., API Class G or H), calcium aluminate cement, sulfur cements, pozzolan cements, lime-silica blends, fly ash, blast furnace slag or zeolites or combinations thereof.

[0049] The cement compositions may further comprise additives for improving or changing the properties thereof. Examples of such additives may include extenders, weighting agents, defoaming agents, foaming surfactants, fluid loss additives (FLAs), gas migration control additives, mechanical property enhancers, antisetling agents, latex emulsions, dispersants or hollow microspheres or combinations thereof.

[0050] Mechanical property modifying additives include elastomers, carbon fibers, glass fibers, metal fibers and mineral fibers. These additives may be included singularly or in combination. Methods for introducing these additives and their effective amounts are known to one of ordinary skill in the art with the aid of this disclosure.

[0051] Extenders include bentonite, unitaite, diatomaceous earth, zeolites and others as are known in the art. Silica powder or silica flour, metakaolin and silica fume may be employed to prevent strength retrogression.

[0052] Defoaming agents have been used in the oil and gas industries to prevent or reduce the formation of foam or the entrainment of gas in well treatment fluids such as cement slurries, oil field drilling mud, oil and gas separation processes, and the like. They provide for better control over the density of the hardened cement that is formed. They have also been used to destroy or "break" previously formed foam in a fluid. For example, a defoaming agent can be added to a well treatment fluid containing foam to break the foam, allowing the fluid to be disposed of more easily. Defoaming agents may include hydrophobic silica, dodecyl alcohol, tributyl phosphate, aluminum stearate, various glycols such as polypropylene glycol, silicones such as polysiloxane emulsions, and sulfonated hydrocarbons.

[0053] FLAs of the presently disclosed and/or claimed concept(s) may include XxtraDura™ FLA 3766 and XxtraDura™ FLA 3767 (available from Ashland Inc.); Polytrol® FL34, Polytrol® FL24 and Alcomer® 244 (available from BASF); FL-14, FL-17, FL-24 (available from Fritz Industries); Halad® 344 (available from Halliburton); UNIFLAC* from Schlumberger; SELVOL™ polyvinyl alcohol (available from Sekisui Specialty Chemicals); carboxymethyl cellulose; carboxy methyl hydroxy ethyl cellulose; xanthan gum; starch; methyl hydroxy ethyl cellulose; propyl hydroxyethyl cellulose; hydroxy ethyl cellulose; guar gum; hydroxy propyl guar; carboxy methyl hydroxy propyl guar; hydroxy ethyl guar; polyvinyl pyrrolidone; and mixtures thereof.

[0054] The FLA described herein typically has a weight average molecular weight (MW) over about 3,000 Daltons, or over about 10,000 Daltons, or over about 100,000 Daltons. In one non-limiting embodiment, the weight average molecular weight is in a range of from about 5,000 to about 5,000,000 Daltons. In another non-limiting embodiment, the weight average molecular weight is in a range of from about 10,000 to about 500,000 Daltons. In yet another non-limiting embodiment, the weight average molecular weight is in a range of from about 50,000 to about 400,000 Daltons. The weight average molecular weight can be determined by GPC techniques that are known in the art.

[0055] The FLA in the presently disclosed and/or claimed concept(s) can be used in either solid or liquid forms. The liquid form can include a liquid FLA and FLA solution. The required amount of FLA in liquid form for the desired composition of the presently disclosed and/or claimed concept(s) can be in a range of from about 0.01 gps (gallons per sack of cement) to about 10 gps, or about 0.1 gps to about 5 gps, or about 0.5 gps to about 1.5 gps. Or, in SI units, about 0.89 L/tonne to about 890L/tonne, or about 8.9 L/tonne to about 445 L/tonne, or about 44.5 L/tonne to about 133 L/tonne. The required amount of FLA in solid form for the desired composition of the presently disclosed and/or claimed concept(s) can be in a range of from about 0.01% to about 10% BWOC (by weight of the cement), or from about 0.1% to about 5.0% BWOC, or from about 0.2 to about 2.0% BWOC.

[0056] The cement material of the presently disclosed and/or claimed concept(s) can also include a defoaming agent (defoamer).

[0057] Gas migration control additives may include styrene-butadiene latexes and polyvinylpyrrolidones and others known in the art.

[0058] Weighting agents may include hematite, barite, ilmenite and manganese tetraoxide, available under different particle sizes.

[0059] The water may be fresh water or salt water, e.g., an unsaturated aqueous salt solution or a saturated aqueous salt solution such as brine or seawater. The water may be present in an amount from about 20 wt% to about 180 wt%, or from about 30 wt% to about 150 wt%, or from about 30 wt% to about 90 wt%, or from about 30wt % to about 60 wt%, by weight of cement. The amount of water may depend on the desired density of the cement slurry and the desired slurry rheology and as such may be determined by one of ordinary skill in the art with the aid of this disclosure.

[0060] Various ingredients described above may be available in solid form, liquid form, suspensions or aqueous solutions. Generally, the cement slurry comprising the cement retarder composition may be made by adding the solid ingredients into the ingredients in liquid forms, suspensions or aqueous solutions.

[0061] In one non-limiting embodiment, the cement retarder composition in solid form can be mixed with other solid ingredients to form a solid mixture. Separately, sufficient water is mixed with the ingredients in liquid forms to form an aqueous solution. The liquid forms include

liquid ingredients and ingredients in solutions. Then the solid mixture is added into the aqueous solution to form a cement slurry. The amounts of the cement retarder composition in the solid mixture can be varied from about 0.1% to about 10% BWOC or from about 0.2% to about 5% BWOC. The retarder composition may further comprise a retarder intensifier comprising borax, sodium pentaborate, an alkanolamine polyborate compound or colloidal silica or a combination thereof. The alkanolamine polyborate may be derived from an alkanolamine comprising monoethanolamine, diethanolamine, triethanolamine, 1-amino-2-propanol or combinations thereof.

[0062] In another non-limiting embodiment, sufficient water is added into the cement retarder composition in aqueous solution and other ingredients in liquid forms to form an aqueous solution. The liquid forms include liquid ingredients and ingredients in solutions. The solid ingredients are then added into the aqueous solution to form a cement slurry. The amounts of the cement retarder composition in aqueous solution may be varied from about 0.1 gpa [8.9 L/tonne) to about 10 gpa (890 L/tonne) or from 0.2 gpa (17.8 L tonne) to about 5 gpa (445 L/tonne).

[0063] In yet a further aspect, embodiments relate to methods for cementing a subterranean well having a wellbore. A composition is prepared that comprises water, a hydraulic cement and a retarder comprising the copolymer of Formula (I) or the copolymer of Formula (VI) or both. The composition is then placed in the wellbore. The placement may be primary cementing or remedial cementing. The retarder composition may further comprise a retarder intensifier comprising borax, sodium pentaborate, an alkanolamine polyborate compound or colloidal silica or a combination thereof. The alkanolamine polyborate may be derived from an alkanolamine comprising monoethanolamine, diethanolamine, triethanolamine, 1-amino-2-propanol or combinations thereof.

[0064] In yet a further aspect, embodiments relate to methods for treating a subterranean well having a wellbore. A composition is prepared that comprises water, a hydraulic cement and a retarder comprising the copolymer of Formula (I) or the copolymer of Formula (VI) or both. The composition is then placed in the wellbore. The placement may be primary cementing or remedial cementing. The retarder composition may further comprise a retarder intensifier comprising borax, sodium pentaborate, an alkanolamine polyborate compound or colloidal silica

or a combination thereof. The alkanolamine polyborate may be derived from an alkanolamine comprising monoethanolamine, diethanolamine, triethanolamine, 1-amino-2-propanol or combinations thereof.

[0065] The weight average molecular weight of the copolymer may be varied from about 1,000 to about 1,000,000 Daltons, or from about 1,500 to about 500,000 Daltons, or from about 2,000 to about 250,000 Daltons, or from about 5,000 to about 150,000 Daltons, or from about 10,000 to about 50,000 Daltons.

[0066] The copolymer may be polymerized from an alpha, beta ethylenically unsaturated carboxylic acid, an unsaturated dicarboxylic acid, hydroxypolyethoxyl allyl ether, and vinyl acetate. The unsaturated dicarboxylic acid may be maleic acid or maleic anhydride.

[0067] In one non-limiting embodiment, the alpha, beta ethylenically unsaturated carboxylic acid may be acrylic acid. In another non-limiting embodiment, the alpha, beta ethylenically unsaturated carboxylic acid may be an (alkyl)acrylic acid such as methacrylic acid.

[0068] The unsaturated dicarboxylic acid can include, but are not limited to, maleic acid, maleic anhydride, fumaric acid, and combinations thereof.

[0069] The cement retarder composition is capable of delaying the set time of the cement slurry until the slurry is placed into its desired location. When used, the set time of the aqueous cement slurry may be delayed during placement at downhole temperatures as high as 315°C. Then, the cement slurry may be hardened to a solid mass at elevated temperatures within the wellbore. Further, the cement slurries used in the presently disclosed and/or claimed concept(s) may exhibit set times at elevated temperatures and pressures even in the absence of an intensifier such as boric acid, borax or boroethanolamine. Other retarder intensifiers may include colloidal silica.

[0070] The hydraulic cement may comprise portland cement (e.g., API Class G or H), calcium aluminate cement, sulfur cements, pozzolan cements, lime-silica blends, fly ash, blast furnace slag or zeolites or combinations thereof.

[0071] The cement compositions may further comprise additives for improving or changing the properties thereof. Examples of such additives may include extenders, weighting agents, defoaming agents, foaming surfactants, fluid loss additives (FLAs), gas migration control

additives, mechanical property enhancers, antisetling agents, latex emulsions, dispersants or hollow microspheres or combinations thereof.

[0072] Mechanical property modifying additives include elastomers, carbon fibers, glass fibers, metal fibers and mineral fibers. These additives may be included singularly or in combination. Methods for introducing these additives and their effective amounts are known to one of ordinary skill in the art with the aid of this disclosure.

[0073] Extenders include bentonite, unitaite, diatomaceous earth, zeolites and others as are known in the art. Silica powder or silica flour, metakaolin and silica fume may be employed to prevent strength retrogression.

[0074] Defoaming agents have been used in the oil and gas industries to prevent or reduce the formation of foam or the entrainment of gas in well treatment fluids such as cement slurries, oil field drilling mud, oil and gas separation processes, and the like. They provide for better control over the density of the hardened cement that is formed. They have also been used to destroy or "break" previously formed foam in a fluid. For example, a defoaming agent can be added to a well treatment fluid containing foam to break the foam, allowing the fluid to be disposed of more easily. Defoaming agents may include hydrophobic silica, dodecyl alcohol, tributyl phosphate, aluminum stearate, various glycols such as polypropylene glycol, silicones such as polysiloxane emulsions, and sulfonated hydrocarbons.

[0075] FLAs of the presently disclosed and/or claimed concept(s) may include XxtraDura™ FLA 3766 and XxtraDura™ FLA 3767 (available from Ashland Inc.); Polytrol® FL34, Polytrol® FL24 and Alcomer® 244 (available from BASF); FL-14, FL-17, FL-24 (available from Fritz Industries); Halad® 344 (available from Halliburton); UNIFLAC* from Schlumberger; SELVOL™ polyvinyl alcohol (available from Sekisui Specialty Chemicals); carboxymethyl cellulose; carboxy methyl hydroxy ethyl cellulose; xanthan gum; starch; methyl hydroxy ethyl cellulose; propyl hydroxyethyl cellulose; hydroxy ethyl cellulose; guar gum; hydroxy propyl guar; carboxy methyl hydroxy propyl guar; hydroxy ethyl guar; polyvinyl pyrrolidone; and mixtures thereof.

[0076] The FLA described herein typically has a weight average molecular weight (MW) over about 3,000 Daltons, or over about 10,000 Daltons, or over about 100,000 Daltons. In one non-limiting embodiment, the weight average molecular weight is in a range of from about 5,000

to about 5,000,000 Daltons. In another non-limiting embodiment, the weight average molecular weight is in a range of from about 10,000 to about 500,000 Daltons. In yet another non-limiting embodiment, the weight average molecular weight is in a range of from about 50,000 to about 400,000 Daltons. The weight average molecular weight can be determined by GPC techniques that are known in the art.

[0077] The FLA in the presently disclosed and/or claimed concept(s) can be used in either solid or liquid forms. The liquid form can include a liquid FLA and FLA solution. The required amount of FLA in liquid form for the desired composition of the presently disclosed and/or claimed concept(s) can be in a range of from about 0.01 gps (gallons per sack of cement) to about 10 gps, or about 0.1 gps to about 5 gps, or about 0.5 gps to about 1.5 gps. Or, in SI units, about 0.89 L/tonne to about 890 L/tonne, or about 8.9 L/tonne to about 445 L/tonne, or about 44.5 L/tonne to about 133 L/tonne. The required amount of FLA in solid form for the desired composition of the presently disclosed and/or claimed concept(s) can be in a range of from about 0.01% to about 10% BWOC (by weight of the cement), or from about 0.1% to about 5.0% BWOC, or from about 0.2 to about 2.0% BWOC.

[0078] The cement material of the presently disclosed and/or claimed concept(s) can also include a defoaming agent (defoamer).

[0079] Gas migration control additives may include styrene-butadiene latexes and polyvinylpyrrolidones and others known in the art.

[0080] Weighting agents may include hematite, barite, ilmenite and manganese tetraoxide, available under different particle sizes.

[0081] The water may be fresh water or salt water, e.g., an unsaturated aqueous salt solution or a saturated aqueous salt solution such as brine or seawater. The water may be present in an amount from about 20 wt% to about 180 wt%, or from about 30 wt% to about 150 wt%, or from about 30 wt% to about 90 wt%, or from about 30 wt% to about 60 wt%, by weight of cement. The amount of water may depend on the desired density of the cement slurry and the desired slurry rheology and as such may be determined by one of ordinary skill in the art with the aid of this disclosure.

[0082] Various ingredients described above may be available in solid form, liquid form, suspensions or aqueous solutions. Generally, the cement slurry comprising the cement retarder

composition may be made by adding the solid ingredients into the ingredients in liquid forms, suspensions or aqueous solutions.

[0083] In one non-limiting embodiment, the cement retarder composition in solid form can be mixed with other solid ingredients to form a solid mixture. Separately, sufficient water is mixed with the ingredients in liquid forms to form an aqueous solution. The liquid forms include liquid ingredients and ingredients in solutions. Then the solid mixture is added into the aqueous solution to form a cement slurry. The amounts of the cement retarder composition in the solid mixture can be varied from about 0.1% to about 10% BWOC or from about 0.2% to about 5% BWOC.

[0084] In another non-limiting embodiment, sufficient water is added into the cement retarder composition in aqueous solution and other ingredients in liquid forms to form an aqueous solution. The liquid forms include liquid ingredients and ingredients in solutions. The solid ingredients are then added into the aqueous solution to form a cement slurry. The amounts of the cement retarder composition in aqueous solution may be varied from about 0.1 gps [8.9 L/tonne) to about 10 gps (890 L/tonne) or from 0.2 gps (17.8 L tonne) to about 5 gps (445 L/tonne).

[0085] The disclosure is further illustrated by the following non-limiting examples.

EXAMPLES

Copolymer Preparation

Example 1

[0086] To a 1L reactor, equipped with a water condenser, temperature controller, N₂ inlet/outlet, and oil bath, was added with 78 g polyethylene glycol allyl ether (Rhodasurf®AAE-10, commercially available from Solvay), 150 g deionized water, and 17.8 g maleic acid to form a homogenous solution. The reactor was then purged with N₂ and the temperature was raised to 75°C. Meanwhile, a monomer solution containing 10 g vinyl acetate, 14 g acrylic acid and 15 g deionized water was prepared. After 30 min purge, the monomer solution and 3.25 g V-50 (2,2'-Azobis(2-methylpropionamidine)dihydrochloride (commercially available from Wako Chemicals USA, Inc.) dissolved in 20 g deionized water were fed into the

reactor from separate pumps over 180 min. After the feeding, the reactor temperature was raised to 80°C for additional 2 hr. The reactor was then cooled down and the solution inside the reactor was discharged into a container. 25 g NaOH solution (50%) was added into the container to neutralize the solution to pH = 6–7. The aqueous solution was used directly in the tests below.

Example 2

[0087] To a 1L reactor, equipped with a water condenser, temperature controller, N₂ inlet/outlet, and oil bath, was added with 78 g Rhodasurf®AAE-10, 60 g deionized water, and 17.8 g maleic acid to form a homogenous solution. The reactor was then purged with N₂ and the temperature was raised to 75°C. Meanwhile, a monomer solution containing 10 g vinyl acetate and 14 g acrylic acid was prepared. After 30 min purge, the monomer solution, and 3.25 g V-50 dissolved in 20 g deionized water were fed into the reactor from separate pumps over 180 min. After the feeding, the reactor temperature was raised to 80°C for additional 2 hr. The reactor was then cooled down and the solution inside the reactor was discharged into a container. 25 g NaOH solution (50%) was added into the container to neutralize the solution to pH = 6-7. The solid sample was then obtained by removing water from the solution and used in the tests below.

Example 3

[0088] To a 1L reactor, equipped with a water condenser, temperature controller, N₂ inlet/outlet, and oil bath, was added with 58.5 g Rhodasurf AAE-10, 50 g deionized water, and 17.8 g maleic acid to form a homogenous solution. The reactor was then purged with N₂ and the temperature was raised to 75°C. Meanwhile, a monomer solution containing 10 g vinyl acetate and 14 g acrylic acid was prepared. After 30 min purge, the monomer solution, and 3.25 g V-50 dissolved in 20 g deionized water were fed into the reactor from separate pumps over 180 min. After the feeding, the reactor temperature was raised to 80°C for additional 2 hr. The reactor was then cooled down and the solution inside the reactor was discharged into a container. 25g NaOH solution (50%) was added into the container to neutralize the solution to pH = 6-7. The solid sample was then obtained by removing water from the solution and used in the tests below.

Testing of The Copolymers

Example 4

[0089] Base slurries were prepared with the following composition: Lafarge Joppa Class H Portland cement, plus silica flour at a concentration of 35% by weight of cement (BWOC). Fresh water was added to prepare slurries with densities of 15.8 lbm/gal, 16.2 lbm/gal and 16.4 lbm/gal (1,900 kg/m³, 1,940 kg/m³ and 1,980 kg/m³). Solid additives were dry blended with the cement before slurry preparation. Liquid additives were added to the water before slurry preparation. The cement slurry compositions are listed in Table 1. FLA-L and FLA-P are fluid-loss additives that are commercially available from Ashland, Inc.

[0090] The slurries were prepared in a Waring blender according to the recommended American Petroleum Institute (API) procedure. The procedure is published in the following publication: *Recommended Practice for Testing Well Cements*, American Petroleum Institute Publication 10B-2, 1st Edition, July 2005.

[0091] The thickening times of the cement slurries were measured in a consistometer according to the API procedure published in API Publication 10B-2. The apparatus was a Model 8340 Single Cell HPHT Consistometer (available from Chandler Engineering, Tulsa, OK, USA). The times at which the slurry viscosities reached 70 Bearden units (Bc) and 100 Bc were recorded as well as the time at which the consistometer shear pin broke.

[0092] Slurries containing the retarders of Examples 1–3 were tested at bottomhole circulating temperatures (BHCTs) between 300°F and 450°F (149°C and 232°C), and the results are presented in Table 1.

[0093] Slurries 1 and 2 were control compositions that did not contain a retarder. The remaining slurries contained one of the retarders described above, and the experimental data illustrate the retarders' ability to increase the thickening times at high BHCTs. Notably, the slurry compositions did not include an intensifier.

[0094] The results also showed that the FLA-L and FLA-P materials have a retarding effect on their own. It is well known in the art that a "neat" cement slurry (i.e., with no retarder or fluid-loss additive) would set before the slurry reached target temperatures as high as 177°C.

Example 5

[0095] A base slurry was prepared with the following composition: Dyckerhoff Class G cement, plus silica flour at a concentration of 40% BWOC. Fresh water was added to prepare a slurry with a density of 15.8 lbm/gal (1,900 kg/m³). All additives (antifoam, FLAs, retarder, retarder aid) were added in the fresh water prior to cement mixing.

[0096] Slurry preparation and thickening time testing was performed in the same manner as that described in Example 4. The slurries were tested at BHCTs between 350°F and 450°F (177°C and 232°C). The results are presented in Table 2.

[0097] In these experiments some of the slurries contained a boron based retarder intensifier—monoethanolamine triborate (MEAT). The MEAT material is SYNTRHO-BORE BL 11%, available from Synthron, Levallois-Perret, France. The results show that the intensifier has the ability to further increase the thickening time significantly.

[0098] From the foregoing, it will be observed that numerous variations and modifications may be effected without departing from the true spirit and scope of the novel concepts of the presently disclosed and/or claimed concept(s).

[0099] Although a few example embodiments have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the example embodiments without materially departing from this disclosure. Accordingly, all such modifications are intended to be included within the scope of this disclosure as defined in the following claims.

Table 1

Slurry Sample	Lafarge Joppa Class H Cement + 35% Silica Flour								Density	BHCT	Ramp	Pressure	Thickening Time		
	HEC	FLA-L	FLA-P	Example 1	Example 2	Example 3	Defoamer	Fresh Water					70 Bc	100 Bc	Shear Pin
	wt%	L/tonne	wt%	wt%	L/tonne	wt%	L/tonne	L/tonne					hr:m	hr:m	hr:m
1	0.6	28.7					0.45	528	1900	177	1:30	7.2–103	2:46	2:46	2:53
2	0.6		1				0.45	546	1900	177	1:30	7.2–103	2:35	2:35	2:36
3	0.5	15.1		0.17			0.45	520	1900	177	0:50	6.9–76.6	14:35	14:36	14:45
4	0.5		0.5		44.5		0.45	539	1900	177	1:50	6.9–76.6	16:26	16:27	16:39
5			0.5		44.5		0.89	490	1940	149	1:14	6.2–76.6	45:34	45:36	45:38
6			0.5		44.5		0.89	490	1940	177	1:22	6.9–89.7	13:52	13:53	13:54
7			0.5		44.5		0.89	455	1980	177	1:22	6.9–89.7	14:06	14:06	14:11
8			0.5		44.5		0.89	455	1980	232	1:30	7.2–103	7:25	7:31	7:32
9	0.6		0.5			0.5	0.45	539	1900	177	1:30	7.2–103	18:33	18:33	18:38
10	0.6		0.625			0.625	0.45	539	1900	232	1:38	7.9–116	6:00	6:03	6:05

- (1) HEC – Hydroxyethyl cellulose, Natrosol™ 250 HHBR, commercially available from Ashland Inc.
- (2) FLA-L – XxtraDura™ FLA 3766, commercially available from Ashland Inc.
- (3) FLA-P – XxtraDura™ FLA 3767, commercially available from Ashland Inc.
- (4) Defoamer - Drewplus™ S-4386, commercially available from Ashland Inc.
- (5) BHCT is referred to Bottom Hole Circulating Temperature

Table 2

Slurry sample	Example 1 %BWOC	Example 2 %BWOC	Example 3 %BWOC	MEAT L/tonne	UNIFLAC™ L/tonne	BHCT (°C)	Ramp (min)	Pressure (MPa)	70 Bc (hr:min)	100 Bc (hr:min)
1	1	—	—	—		177	90	104	1:48	1:50
2	1.5	—	—	—		177	90	104	2:25	2:27
3	—	2	—	—		177	90	104	3:20	3:20
4	—	—	1	—		177	90	104	1:52	1:54
5	1	—	—	17.8		177	90	104	24:00	24:03
6	1	—	—	17.8		232	90	104	18:19	18:20
7	—	—	1	17.8		177	90	104	3:50	3:50
8	—	—	1	24.0		177	90	104	43:25	43:25
9	—	—	1	24.0		232	90	104	27:37	27:37

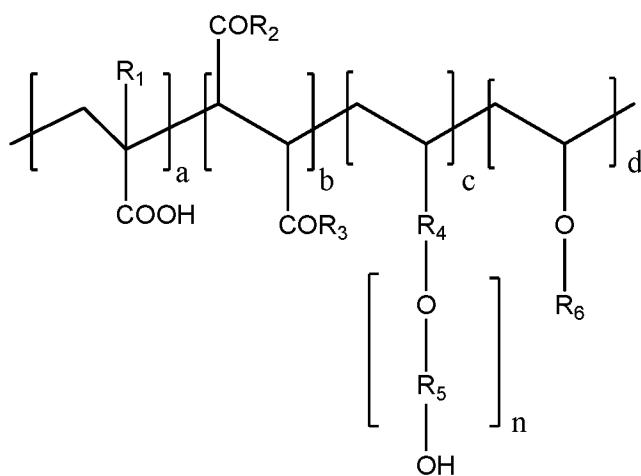
What is claimed is:

1. A composition, comprising:

(i) water;

(ii) a hydraulic cement; and

(iii) a retarder comprising a copolymer represented by Formula (I):



Formula (I)

wherein:

R₁ is hydrogen, or straight or branched C₁-C₅ alkyl;

R₂ and R₃ are independently OH or NH₂;

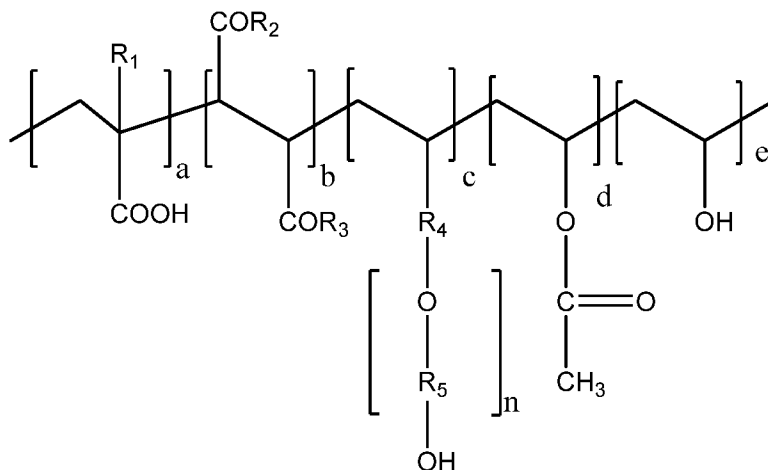
R₄ is C=O, or independently straight or branched C₁-C₅ alkyl;

R₅ is independently straight or branched C₁-C₅ alkyl;

R₆ is hydrogen or COR₇, wherein R₇ is straight or branched C₁-C₅ alkyl; and

n is an integer from 1 to 100; or

a copolymer represented by Formula (VI):



Formula (VI)

wherein:

R_1 is hydrogen, or straight or branched C_1 - C_5 alkyl;

R_2 and R_3 are independently OH or NH_2 ;

R_4 is $C=O$ or independently straight or branched C_1 - C_5 alkyl;

R_5 is independently straight or branched C_1 - C_5 alkyl; and

n is an integer from 1 to 100, or both.

2. The composition of claim 1, wherein the copolymer has a weight average molecular weight between 1,000 and 1,000,000 Daltons.
3. The composition of claim 1, wherein the copolymer is polymerized from an alpha, beta ethylenically unsaturated carboxylic acid, an unsaturated dicarboxylic acid, hydroxypolyethoxyl allyl ether, and vinyl acetate.
4. The composition of claim 3, wherein the unsaturated dicarboxylic acid is maleic acid or maleic anhydride.
5. The composition of claim 1, wherein the alpha, beta ethylenically unsaturated carboxylic acid is acrylic acid or alkylacrylic acid.
6. The composition of claim 1, wherein the alkylacrylic acid is methacrylic acid.

7. The composition of claim 1, further comprising one or more additives selected from the group consisting of silica, metakaolin, bentonite, uintaite, diatomaceous earth, zeolites, a fluid-loss additive, a defoaming agent, an antifoam agent, a foaming surfactant, a weighting material, a latex emulsion, a dispersant, an antisetling agent, a gas migration control additive, a mechanical property enhancer, hollow microspheres and a retarder intensifier comprising boric acid, borax, an alkanolamine polyborate compound or colloidal silica or combinations thereof.

8. The composition of claim 1, wherein the hydraulic cement comprises one or more members of the list consisting of portland cement, calcium aluminate cement, lime-silica blends, sulfur cements, pozzolan cements, fly ash, blast furnace slag and zeolites.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/042727**A. CLASSIFICATION OF SUBJECT MATTER****C09K 8/46(2006.01)i, C09K 8/467(2006.01)i, C09K 8/04(2006.01)i**

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K 8/46; C08F 22/26; C08F 220/64; C04B 24/04; C04B 24/12; C04B 28/14; C08F 220/04; C04B 28/26; C04B 24/00; C09K 8/467; C09K 8/04

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: hydraulic cement, water, retarder, copolymer, acrylic acid, maleic acid, hydropolyethoxyl allyl ether, vinyl acetate, α,β -ethylenically unsaturated carboxylic acid, unsaturated dicarboxylic acid**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6444747 B1 (CHEN, F. et al.) 03 September 2002 See column 1, line 66 - column 3, line 24; column 5, lines 64-66.	1-8
A	US 2015-0152007 A1 (NIPPON SHOKUBAI CO., LTD.) 04 June 2015 See claims 1 and 10.	1-8
A	US 5536311 A (RODRIGUES, K. A.) 16 July 1996 See claims 1-5.	1-8
A	US 5421879 A (RODRIGUES, K. A.) 06 June 1995 See claims 1-6.	1-8
A	US 2006-0081155 A1 (CHATTERJI, J. et al.) 20 April 2006 See claims 1-20.	1-8
L	Application No. PCT/US2016/042715 (SCHLUMBERGER TECHNOLOGY CORPORATION et al.) Application date: 18 July 2016	1-8



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

"E" earlier application or patent but published on or after the international filing date

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

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

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

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

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

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