AQUEOUS-BASED INSULATING FLUIDS AND RELATED METHODS

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Appl. No.: 12/046,086
Filed: Mar. 11, 2008

Related U.S. Application Data
Continuation-in-part of application No. 11/685,909, filed on Mar. 14, 2007.

Base Fluids % by Vol
Fresh Water, (FW) 1 to 60
Monovalent Brines 1 to 60
Divalent Brines 1 to 60
Propylene Glycol, (PG) 40 to 99
Ethylene Glycol, (EG) 40 to 99
Glycerol 40 to 99

Polymers % Wt
Polyacrylamide (M.W. 5-10 x 10⁶ g/mol), (PAM) 0.1 to 5
Polyacrylamide copolymer A (M.W. 6 x 10⁶ g/mol) 0.1 to 5
Polyacrylamide copolymer B (M.W. 2.6 x 10⁶ g/mol) 0.1 to 5
Polyacrylamide terpolymer C (M.W. 0.2-1 x 10⁶ g/mol) 0.1 to 5

System 1 Crosslinkers (primary)
Hydroquinone, (HQ) 500-7000
Phenol 500-7000
Aspirin 500-7000
Phenyl Acetate 500-7000
Amino-benzoic Acid, (ABA) 500-7000
Anthranillic Acid 500-7000

System 1 Crosslinkers (secondary)
Hexamethylenetetramine, (HMTA) 500-7000
Formaldehyde, (FM) 500-7000

System 2 Crosslinker % by Wt
Polyethylenimine (PEI) 0.005 to 10 %
Polyalkylimine 0.005 to 10 %

ABSTRACT

Provided herein are methods and compositions that include a method comprising providing an annulus between a first tubing and a second tubing; providing an aqueous-based insulating fluid that comprises an aqueous base fluid, a water-miscible organic liquid, and a layered silicate; and placing the aqueous-based insulating fluid in the annulus. A composition provided includes an aqueous-based insulating fluid comprising an aqueous base fluid, a water-miscible organic liquid, and a layered silicate.
Polyacrylamide copolymer B (Mw 2025x 16 g/mol) 0.1 to 5
Polyacrylamide copolymer A (M.W. 510 x 10^6 g/mol) 0.1 to 5
Polyacrylamide copolymer B (MW 2.02.5 x 10^6 g/mol) 0.1 to 5
Polyacrylamide terpolymer C (MW 0.2- 10^6 g/mol) 0.1 to 5

System 1 Crosslinkers
- Hydroquinone, (HQ) 500-7000 ppm
- Phenol 500-7000 ppm
- Aspirin 500-7000 ppm
- Phenyl Acetate 500-7000 ppm
- Amino-benzoic Acid, (ABA) 500-7000 ppm
- Antranillic Acid 500-7000 ppm

System 1 Crosslinkers (secondary)
- Hexamethylenetetramine, (HMTA) 500-7000 ppm
- Formaldehyde, (FM) 500-7000 ppm

System 2 Crosslinker
- Polyethylenimine (PEI) .0005 to 10 %
- Polyalkylimine .0005 to 10 %
<table>
<thead>
<tr>
<th>Base Fluids</th>
<th>% by Vol</th>
</tr>
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<tbody>
<tr>
<td>Fresh Water, (FW)</td>
<td>1 to 60</td>
</tr>
<tr>
<td>Monovalent Brines</td>
<td>1 to 60</td>
</tr>
<tr>
<td>Divalent Brines</td>
<td>1 to 60</td>
</tr>
<tr>
<td>Propylene Glycol, (PG)</td>
<td>40 to 99</td>
</tr>
<tr>
<td>Ethylene Glycol, (EG)</td>
<td>40 to 99</td>
</tr>
<tr>
<td>Glycerol</td>
<td>40 to 99</td>
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<table>
<thead>
<tr>
<th>Viscosifiers/Gellants</th>
<th>% Wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic Silicates</td>
<td>0.1 to 5</td>
</tr>
</tbody>
</table>

**FIG. 3**
FIG. 4
AQUEOUS-BASED INSULATING FLUIDS AND RELATED METHODS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation in part of U.S. patent application Ser. No. 11/685,909 entitled “Improved Aqueous-Based Insulating Fluids and Related Methods,” filed on Mar. 14, 2007, the entirety of which is herein incorporated by reference, and from which priority is claimed pursuant to 35 U.S.C. §120.

BACKGROUND

[0002] The present invention relates to insulating fluids, and more particularly, to aqueous-based insulating fluids that have greater stability at high temperatures with lower thermal conductivity that may be used, for example, in applications requiring an insulating fluid such as pipeline and subterranean applications (e.g., to insulate petroleum production conduits).

[0003] Insulating fluids are often used in subterranean operations wherein the fluid is placed into an annulus between a first tubing and a second tubing or the walls of a well bore. The insulating fluid acts to insulate a first fluid (e.g., a hydrocarbon fluid) that may be located within the first tubing from the environment surrounding the first tubing or the second tubing to enable optimum recovery of the hydrocarbon fluid. For instance, if the surrounding environment is very cold, the insulating fluid is thought to protect the first fluid in the first tubing from the environment so that it can efficiently flow through the production tubing, e.g., the first tubing, to other facilities. This is desirable because heat transfer can cause problems such as the precipitation of heavier hydrocarbons, severe reductions in flow rate, and in some cases, casing collapse. Additionally, when used in packer applications, a required amount of hydrostatic head pressure is needed. Thus, higher density insulating fluids are often used for this reason as well to provide the requisite hydrostatic force.

[0004] Such fluids also may be used for similar applications involving pipelines for similar purposes, e.g., to protect a fluid located within the pipeline from the surrounding environmental conditions so that the fluid can efficiently flow through the pipeline. Insulating fluids may be used in other insulating applications as well wherein it is desirable to control heat transfer. These applications may or may not involve hydrocarbons.

[0005] Beneficial insulating fluids preferably have a low inherent thermal conductivity, and also should remain gelled to prevent, inter alia, convection currents that could carry heat away. Additionally, preferred insulating fluids should be aqueous-based, and easy to handle and use. Moreover, preferred fluids should tolerate ultra high temperatures (e.g., temperatures of 400°F or above) for long periods of time for optimum performance.

[0006] Conventional aqueous-based insulating fluids have been subject to many drawbacks. First, many have associated temperature limitations. Typically, most aqueous-based insulating fluids are only stable up to 240°F for relatively short periods of time. This can be problematic because it can result in premature degradation of the fluid, which can cause the fluid not to perform its desired function with respect to insulating the first fluid. A second common limitation of many conventional aqueous-based insulating fluids is their density range. Typically, these fluids have an upper density limit of 12.5 ppg. oftentimes, higher densities are desirable to maintain adequate pressure for the chosen application. Additionally, most aqueous-based insulating fluids have excessive thermal conductivities, which means that these fluids are not as efficient or effective at controlling conductive heat transfer. Moreover, when a viscosified fluid is required to eliminate convective currents, oftentimes to obtain the required viscosity in current aqueous-based fluids, the fluids may become too thick to be able to pump into place. Some aqueous-based fluids also can have different salt tolerances that may not be compatible with various brines used, which limits the operators’ options as to what fluids to use in certain circumstances.

[0007] In some instances, insulating fluids may be oil-based. Certain oil-based fluids may offer an advantage because they may have lower thermal conductivity as compared to their aqueous counterparts. However, many disadvantages are associated with these fluids as well. First, oil-based insulating fluids can be hard to “weight up,” meaning that it may be hard to obtain the necessary density required for an application. Secondly, oil-based fluids may present toxicity and other environmental issues that must be managed, especially when such fluids are used in subsea applications. Additionally, there can be interface issues if aqueous completion fluids are used. Another complication presented when using oil-based insulating fluids is the concern about their compatibility with any elastomeric seals that may be present along the first tubing line.

[0008] Another method that may be employed to insulate a first tubing involves using vacuum insulated tubing. However, this method also can present disadvantages. First, when the vacuum tubing is installed on a completion string, sections of the vacuum tubing can fail. This can be a costly problem involving a lot of down time. In severe cases, the first tubing can collapse. Secondly, vacuum insulated tubing can be very costly and hard to place. Moreover, in many instances, heat transfer at the junctions or connective joints in the vacuum tubings can be problematic. These may lead to “hot spots” in the tubings.

SUMMARY

[0009] The present invention relates to insulating fluids, and more particularly, to aqueous-based insulating fluids that have greater stability at high temperatures with lower thermal conductivity that may be used, for example, in applications requiring an insulating fluid such as pipeline and subterranean applications (e.g., to insulate petroleum production conduits).

[0010] In one embodiment, the present invention provides a method comprising: providing an annulus between a first tubing and a second tubing; providing an aqueous-based insulating fluid that comprises an aqueous base fluid, a water-miscible organic liquid, and a layered silicate; and placing the aqueous-based insulating fluid in the annulus. In some embodiments, the aqueous-based insulating fluid also includes a polymer.

[0011] In one embodiment, the present invention provides a method comprising: providing a tubing containing a first fluid located within a well bore such that an annulus is formed between the tubing and a surface of the well bore; providing an aqueous-based insulating fluid that comprises an aqueous base fluid, a water-miscible organic liquid, and a layered...
silicate; and placing the aqueous-based insulating fluid in the annulus. In some embodiments, the aqueous-based insulating fluid also includes a polymer.

[0012] In one embodiment, the present invention provides a method comprising: providing a first tubing that comprises at least a portion of a pipeline that contains a first fluid; providing a second tubing that substantially surrounds the first tubing thus creating an annulus between the first tubing and the second tubing; providing an aqueous-based insulating fluid that comprises an aqueous base fluid, a water-miscible organic liquid, and a layered silicate; and placing the aqueous-based insulating fluid in the annulus. In some embodiments, the aqueous-based insulating fluid also includes a polymer.

[0013] In one embodiment, the present invention provides an aqueous-based insulating fluid that comprises an aqueous base fluid, a water-miscible organic liquid, and a layered silicate. In some embodiments, the aqueous-based insulating fluid also includes a polymer.

[0014] In another embodiment, the present invention provides a method of forming an aqueous-based insulating fluid comprising: mixing an aqueous base fluid and a water-miscible organic liquid to form a mixture; adding at least one layered silicate to the mixture; allowing the silicate to hydrate; placing the mixture comprising the layered silicate in a chosen location; allowing the mixture comprising the layered silicate to activate to form a gel therein. In some embodiments, a polymer may be added to the mixture and allowed to hydrate. Optionally, a crosslinking agent may be added to the mixture comprising the polymer to crosslink the polymer.

[0015] The features and advantages of the present invention will be readily apparent to those skilled in the art. While numerous changes may be made by those skilled in the art, such changes are within the spirit of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] These drawings illustrate certain aspects of some of the embodiments of the present invention, and should not be used to limit or define the invention.

[0017] FIG. 1 lists the materials used in the formulations and the amounts thereof as described in Example 1 in the Examples section.

[0018] FIG. 2 illustrates data from a fluid that was heated to about 190°F for 5000 minutes to activate the crosslinking agent and provide an increase in viscosity.

[0019] FIG. 3 lists the materials that may be used in the formulations and the approximate amounts thereof as described in Example 2 in the Examples section.

[0020] FIG. 4 illustrates data from a fluid that was heated from approximately 100°F to approximately 600°F for approximately 45,000 seconds at approximately 10,000 psi.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0021] The present invention relates to insulating fluids, and more particularly, to aqueous-based insulating fluids that have greater stability at high temperatures with lower thermal conductivity that may be used, for example, in applications requiring an insulating fluid such as pipeline and subterranean applications (e.g., to insulate petroleum production conduits). The aqueous-based insulating fluids of the present invention may be used in any application requiring an insulating fluid. Preferably, they may be used in pipeline and subterranean applications.

[0022] The improved aqueous-based insulating fluids and methods of the present invention present many potential advantages, only some of which are alluded to herein. One of these many advantages is that the fluids may have enhanced thermal stability, which enables them to be beneficially used in many applications. Secondly, in some embodiments, the aqueous-based insulating fluids of the present invention may have higher densities than conventional aqueous-based insulating fluids, and therefore, present a distinct advantage in that respect. Additionally, the aqueous-based insulating fluids of the present invention have relatively low thermal conductivity, which is thought to be especially beneficial in certain applications. In some embodiments, these fluids are believed to be very durable. Moreover, in some embodiments, the fluids of the present invention offer aqueous-based viscous insulating fluids with a broad fluid density range, decreased thermal conductivity, and stable gel properties at temperatures exceeding those of current industry standards (e.g., even at temperatures of about 600°F or more, depending on the organic liquid included). Another potential advantage is that these fluids may prevent the formation of hydrates within the insulating fluids themselves or the fluids being insulated. Other advantages and objects of the invention may be apparent to one skilled in the art with the benefit of this disclosure.

[0023] In certain embodiments, the aqueous-based insulating fluids of the present invention comprise an aqueous base fluid, a water-miscible organic liquid, and a layered silicate. In certain embodiments, the aqueous-based insulating fluids of the present invention comprise an aqueous base fluid, a water-miscible organic liquid, a layered silicate, and optionally a synthetic polymer. In some instances, the polymer may be crosslinked by using or adding to the fluid an appropriate crosslinking agent. Thus, the term “polymer” as used herein refers to oligomers, copolymers, terpolymers and the like, which may or may not be crosslinked. Optionally, the aqueous-based insulating fluids of the present invention may comprise other additives such as corrosion inhibitors, pH modifiers, biocides, glass beads, hollow spheres (e.g., hollow microspheres), rheology modifiers, buffers, hydrate inhibitors, breakers, tracers, additional weighting agents, viscosifiers, surfactants, and combinations of any of these. Other additives may be appropriate as well and beneficially used in conjunction with the aqueous-based insulating fluids of the present invention as may be recognized by one skilled in the art with the benefit of this disclosure.

[0024] The aqueous base fluids that may be used in the aqueous-based insulating fluids of the present invention include any aqueous fluid suitable for use in insulating, subterranean, or pipeline applications. In some instances, brines may be used, for example, when a relatively denser aqueous-based insulating fluid is desired (e.g., density of 10.5 ppg or greater); however, it may be observed that the fluids of the present invention may be less tolerant to higher concentrations of salts than other fluids, such as those that include a polymer as described herein but not a layered silicate as described herein. Suitable brines include, but are not limited to, NaCl, NaBr, KCl, CaCl₂, CaBr₂, ZrBr₄, sodium carbonate, sodium formate, potassium formate, cesium formate, and combinations and derivatives of these brines. Others may be appropriate as well. The specific brine used may be dictated by the desired density of the resulting aqueous-based insulat-
ing fluid or for compatibility with other completion fluid brines that may be present. Denser brines may be useful in some instances. A density that is suitable for the application at issue should be used as recognized by one skilled in the art with the benefit of this disclosure. When deciding how much of an aqueous fluid to include, a general guideline to follow is that the aqueous fluid component should comprise the balance of a high temperature aqueous-based insulating fluid after considering the amount of the other components present therein.

**[0025]** The water-miscible organic liquids that may be included in the aqueous-based insulating fluids of the present invention include water-miscible materials having relatively low thermal conductivity (e.g., about half as conductive as water or less). By “water-miscible,” it is meant that about 5 grams or more of the organic liquid will disperse in 100 grams of water. Suitable water-miscible organic liquids include, but are not limited to, esters, amines, alcohols, polyols, glycol ethers, or combinations and derivatives of these. Examples of suitable esters include low molecular weight esters; specific examples include, but are not limited to, methylformate, methyl acetate, and ethyl acetate. Combinations and derivatives are also suitable. Examples of suitable amines include low molecular weight amines; specific examples include, but are not limited to, diethylanmine, 2-aminoethanol, and 2-(dimethylamino)ethanol. Combinations and derivatives are also suitable. Examples of suitable alcohols include methanol, ethanol, propanol, isopropanol, and the like. Combinations and derivatives are also suitable. Examples of glycol ethers include ethylene glycol butyl ether, diethylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, and the like. Combinations and derivatives are also suitable. Of these, polyols are generally preferred in most cases over the other liquids since they generally are thought to exhibit greater thermal and chemical stability, higher flash point values, and are more benign with respect to elastomeric materials.

**[0026]** Suitable polyols are those aliphatic alcohols containing two or more hydroxy groups. It is preferred that the polyol be at least partially water-miscible. Examples of suitable polyols that may be used in the aqueous-based insulating fluids of this invention include, but are not limited to, water-soluble diols such as ethylene glycols, propylene glycols, polyethylene glycols, polypropylene glycols, diethylene glycols, triethylene glycols, dipropylene glycols and tripropylene glycols, combinations of these glycols, their derivatives, and reaction products formed by reacting ethylene and propylene oxide or polyethylene glycols and polypropylene glycols with active hydrogen base compounds (e.g., polyalcohols, polycarboxylic acids, polyamines, or polyphenols). The polyglycols of ethylene generally are thought to be water-miscible at molecular weights at least as high as 20,000. The polyglycols of propylene, although giving slightly better grinding efficiency than the ethylene glycols, are thought to be water-miscible up to molecular weights of only about 1,000. Other glycols possibly contemplated include neopentyl glycol, pentanediols, butanediols, and such unsaturated diols as butyne diols and butene diols. In addition to the diols, the triols, glycerol, and such derivatives as ethylene or propylene oxide adducts may be used. Other higher polyols may include pentaerythritol. Another class of polyhydroxy alcohols contemplated is the sugar alcohols. The sugar alcohols are obtained by reduction of carbohydrates and differ greatly from the above-mentioned polyols. Combinations and derivatives of these are suitable as well.

**[0027]** The choice of polyol to be used is largely dependent on the desired density of the fluid. Other factors to consider include thermal conductivity. For higher density fluids (e.g., 10.5 ppg or higher), a higher density polyol may be preferred, for instance, triethylene glycol or glycerol may be desirable in some instances. For lower density applications, ethylene or propylene glycol may be used. In some instances, more salt may be necessary to adequately weight the fluid to the desired density. In certain embodiments, the amount of polyol that should be used may be governed by the thermal conductivity ceiling of the fluid and the desired density of the fluid. If the thermal conductivity ceiling is 0.17 BTU/h ft² F., then the concentration of the polyol may be from about 40% to about 99% of a high temperature aqueous-based insulating fluid of the present invention. A more preferred range could be from about 70% to about 99%.

**[0028]** Examples of layered silicates that may be suitable for use in the present invention include, but are not limited to, smectite, vermiculite, swellable fluoromica, montmorillonite, beidellite, hectorite, and saponite. A high-temperature, electrolyte stable synthetic hectorite may be particularly useful in some embodiments. An example of a synthetic hectorite clay for use in accordance with this invention is “LAPO-NITE™ RD” commercially available from Laporte Absorbents Company of Cheshire, United Kingdom. Mixtures of any of these of silicates may be suitable as well. In preferred embodiments, the silicate may be at least partially water soluble. In some embodiments, the layered silicate may be a natural layered silicate or a synthetic layered silicate. In certain embodiments, the silicate should comprise from about 0.1% to about 15% weight by volume of the fluid, and more preferably, from about 0.5% to about 4% weight by volume of the fluid.

**[0029]** Inclusion of a synthetic polymer may be useful, inter alia, to produce fluids that exhibit gelation behavior. Examples of synthetic polymers that optionally may be suitable for use in the present invention include, but are not limited to, acrylic acid polymers, acrylate acid ester polymers, acrylic acid derivative polymers, acrylic acid homopolymers, acrylic acid ester homopolymers (such as poly(methyl acrylate)), poly(acryl acrylate), and poly(2-ethylhexyl acrylate)), acrylic acid ester co-polymers, methacrylic acid derivative polymers, methacrylic acid homopolymers, methacrylic acid ester homopolymers (such as poly(methyl methacrylate), polyacrylamide homopolymer, n-vinyl pyrrolidone and polyacrylamide copolymers, poly(butyl methacrylate), and poly (2-ethylhexyl methacrylate)), n-vinyl pyrrolidone, acrylamido-methyl-propene sulfonate polymers, acrylamido-methyl-propene sulfonate derivative polymers, acrylamido-methyl-propene sulfonate co-polymers, and acrylic acidpolyamido-methyl-propene sulfonate copolymers, and combinations thereof. Copolymers and terpolymers may be suitable as well. Mixtures of any of these of polymers may be suitable as well. In preferred embodiments, the polymer should be at least partially water soluble. Suitable polymers can be cationic, anionic, nonionic, or zwitterionic. In certain embodiments, the polymer should comprise from about 0.1% to about 15% weight by volume of the fluid, and more preferably, from about 0.5% to about 4%.

**[0030]** To obtain the desired gel characteristics and thermal stability for an aqueous-based insulating fluid of the present invention, the polymer included in the fluid may be
crosslinked by an appropriate crosslinking agent. In those embodiments of the present invention wherein it is desirable to crosslink the polymer, optionally and preferably, one or more crosslinking agents may be added to the fluid to crosslink the polymer.

[0031] One type of suitable crosslinking agent is a combination of a phenolic component (or a phenolic precursor) and formaldehyde (or formaldehyde precursor). Suitable phenolic components or phenolic precursors include, but are not limited to, phenols, hydroquinone, salicylic acid, salicylamide, aspirin, methyl-p-hydroxybenzoate, phenyl acetate, phenyl salicylate, o-aminobenzoic acid, p-aminobenzoic acid, m-aminophenol, furfuryl alcohol, and benzoic acid. Suitable formaldehyde precursors may include, but are not limited to, hexamethylenetetramine, glyoxal, and 1,3,5-trioxane. This crosslinking agent system needs approximately 250°F to thermally activate to crosslink the polymer. Another type of suitable crosslinking agent is polyacrylimine. This crosslinking agent needs approximately 90°F to activate to crosslink the polymer. This crosslinking agent may be used alone or in conjunction with any of the other crosslinking agents discussed herein.

[0032] Another type of crosslinking agent that may be used includes non-toxic organic crosslinking agents that are free from metal ions. Examples of such organic cross-linking agents are polyalkyleneimines (e.g., polyethyleneimine), polyalkylene polyamines and mixtures thereof. In addition, water-soluble polyfunctional aliphatic amines, aryalkylamines and heteroaryalkylamines may be utilized.

[0033] When included, suitable crosslinking agents may be present in the fluids of the present invention in an amount sufficient to provide, inter alia, the desired degree of crosslinking. In certain embodiments, the crosslinking agent or agents may be present in the fluids of the present invention in an amount in the range of from about 0.0005% to about 10% weight by volume of the fluid. In certain embodiments, the crosslinking agent may be present in the fluids of the present invention in an amount in the range of from about 0.001% to about 5% weight by volume of the fluid. One of ordinary skill in the art, with the benefit of this disclosure, will recognize the appropriate amount of crosslinking agent to include in a fluid of the present invention based on, among other things, the temperature conditions of a particular application, the type of polymer(s) used, the molecular weight of the polymer(s), the desired degree of viscosification, and/or the pH of the fluid.

[0034] Although any suitable method for forming the insulating fluid of the present invention may be used, in some embodiments, an aqueous-based insulating fluid of the present invention may be formulated at ambient temperature and pressure conditions by mixing water and a chosen water-miscible organic liquid. The water and water-miscible organic liquid preferably may be mixed so that the water-miscible organic liquid is miscible in the water. The chosen silicate may then be added and mixed into the water and water-miscible organic liquid mixture until the silicate is hydrated. Any chosen additives may be added at any, including a polymer. Preferably, any additives are dispersed within the mixture. If desired, a crosslinking agent may be added. If used, it should be dispersed in the mixture. Crosslinking, however, generally should not take place until thermal activation, which preferably, in subterranean applications, occurs downhole; this may alleviate any pumping difficulties that might arise as a result of activation before placement. Activation results in the fluid forming a gel. The term “gel,” as used herein, and its derivatives refer to a semi-solid, jelly-like state assumed by some colloidal dispersions. Once activated, the gel should stay in place and be durable with negligible syneresis.

[0035] In some embodiments, the gels formed by hydrating the silicate may have a zero shear viscosity of about 100,000 centipoise measured on an Anton Paar Controlled Stress Rheometer at standard conditions using standard operating procedure.

[0036] Once gelled, if the fluid contains polymer, one method of removing the gel may comprise diluting or breaking the crosslinks and/or the polymer structure within the gel using an appropriate method and/or composition to allow recovery or removal of the gel. Another method could involve physical removal of the gel by, for example, air or liquid.

[0037] In some embodiments, the aqueous-based insulating fluids of the present invention may be prepared on-the-fly at a well-site or pipeline location. In other embodiments, the aqueous-based insulating fluids of the present invention may be prepared off-site and transported to the site of use. In transporting the fluids, one should be mindful of the activation temperature of the fluid.

[0038] In one embodiment, the present invention provides a method comprising: providing a first tubing; providing a second tubing that substantially surrounds the first tubing thus creating an annulus between the first tubing and the second tubing; providing an aqueous-based insulating fluid that comprises an aqueous base fluid, a polyol, and a layered silicate; and placing the aqueous-based insulating fluid in the annulus. In some embodiments, the aqueous-based insulating fluid also includes a polymer. The tubings may have any shape appropriate for a chosen application. In some instances, the second tubing may not be the same length as the first tubing. In some instances, the tubing may comprise a portion of a larger apparatus. In some instances, the aqueous-based insulating fluid may be in contact with the entire first tubing from end to end, but in other situations, the aqueous-based insulating fluid may only be placed in a portion of the annulus and thus only contact a portion of the first tubing. In some instances, the first tubing may be production tubing located within a well bore. In some instances, the tubings may be located in a geothermal well bore. The production tubing may be located in an off-shore location. In other instances, the production tubing may be located in a cold climate. In other instances, the first tubing may be a pipeline capable of transporting a fluid from one location to a second location.

[0039] In one embodiment, the present invention provides a method comprising: providing a first tubing; providing a second tubing that substantially surrounds the first tubing thus creating an annulus between the first tubing and the second tubing; providing an aqueous-based insulating fluid that comprises an aqueous base fluid, a water-miscible organic liquid, and a layered silicate; and placing the aqueous-based insulating fluid in the annulus. In some embodiments, the aqueous-based insulating fluid also includes a polymer.

[0040] In one embodiment, the present invention provides a method comprising: providing a tubing containing a first fluid located within a well bore such that an annulus is formed between the tubing and a surface of the well bore; providing an aqueous-based insulating fluid that comprises an aqueous base fluid, a water-miscible organic liquid, and a layered
silicate; and placing the aqueous-based insulating fluid in the annulus. In some embodiments, the aqueous-based insulating fluid also includes a polymer.

[0041] In one embodiment, the present invention provides a method comprising: providing a first tubing that comprises at least a portion of a pipeline that contains a first fluid; providing a second tubing that substantially surrounds the first tubing thus creating an annulus between the first tubing and the second tubing; providing an aqueous-based insulating fluid that comprises an aqueous base fluid, a water-miscible organic liquid, and a layered silicate; and placing the aqueous-based insulating fluid in the annulus. In some embodiments, the aqueous-based insulating fluid also includes a polymer.

[0042] In one embodiment, the present invention provides an aqueous-based insulating fluid that comprises an aqueous base fluid, a water-miscible organic liquid, and a layered silicate. In some embodiments, the aqueous-based insulating fluid also includes a polymer.

[0043] In another embodiment, the present invention provides a method of forming an aqueous-based insulating fluid comprising: mixing an aqueous base fluid and a water-miscible organic liquid to form a mixture; adding at least one layered silicate to the mixture; allowing the layered silicate to hydrate; placing the mixture comprising the layered silicate in a chosen location; allowing the mixture comprising the layered silicate to actuate to form a gel therein. In some embodiments, a polymer may be added to the mixture and allowed to hydrate. Optionally, a crosslinking agent may be added to the mixture comprising the polymer to crosslink the polymer.

[0044] To facilitate a better understanding of the present invention, 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 invention.

EXAMPLES

[[(Ryan—Confirm that These Examples were Performed Exactly as Written Below)]]

Example 1

[0045] We studied the formulation and testing of various combinations of inorganic, organic, clay and polymeric materials for use as viscosifying/gelling agents in aqueous based fluids for insulating fluids. We conducted a series of tests in which the solubility, thermal conductivity, thermal stability, pH, gelling properties, rheological behavior, and toxicity of the various fluids were evaluated and compared. Perhaps most importantly, the thermal stability ranges from 37° F. to 280° F. and above were evaluated. These tests were conducted over short and long term periods. FIG. 1 lists the materials used in the formulations and the amounts tested. This in no way should be construed as an exhaustive example with reference to the invention or as a definition of the invention in any way.

[0046] Thermal stability and static aging: All formulations of fluids were statically aged at temperatures of about 280° F. for two months. Formulations and properties for the tested fluids are shown in Tables 1 and 2 below. Most of the fluids appeared to remain intact, with the crosslinked systems showing an increase in viscosity and what appeared to be complete gelation behavior. We believe that these systems appeared to exhibit more desirable stability properties than other fluids, which included numerous biopolymers (e.g., xanthan, welan, and diutan gums) and inorganic clays and were generally destroyed after 3 days at 250° F. In addition, as to the thermal stability of these formulations tested, less than 1% syneresis was observed for any of the samples.

[0047] In addition to the static tests, Sample 4 was evaluated using a high-temperature viscometer to examine the thermal activation of crosslinking agents (FIG. 2). The fluid was subjected to a low shear rate at 190° F., with viscosity measurements showing an increase with time to reach the maximum recordable level around 5000 minutes.

<table>
<thead>
<tr>
<th>TABLE 1</th>
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<tr>
<td><strong>IPF Formulations and Properties Before Static Aging.</strong></td>
</tr>
<tr>
<td><strong>Sample</strong></td>
</tr>
<tr>
<td>Density, ppm</td>
</tr>
<tr>
<td>Water, % vol</td>
</tr>
<tr>
<td>Glycerol, % vol</td>
</tr>
<tr>
<td>PC, % vol</td>
</tr>
<tr>
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<tr>
<td>Polymer B, % wt</td>
</tr>
<tr>
<td>Alddehyde, ppm</td>
</tr>
<tr>
<td>HQ, ppm</td>
</tr>
<tr>
<td>PEG, % wt</td>
</tr>
<tr>
<td><strong>Properties</strong></td>
</tr>
<tr>
<td>300 ppm</td>
</tr>
<tr>
<td>Shear Strength, lb/100 ft²</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
</tr>
<tr>
<td>BTU/ft²F</td>
</tr>
</tbody>
</table>

1Measurements obtained from reading observed on Fann 35 viscometer, sample temperature 120° F.

2Measurements obtained by KD2-Pro Thermal Properties Analyzer.

<table>
<thead>
<tr>
<th>TABLE 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>IPF Formulations and Properties After 60 Days Static Aging at 280° F.</strong></td>
</tr>
<tr>
<td><strong>Sample</strong></td>
</tr>
<tr>
<td>Density, ppm</td>
</tr>
<tr>
<td>Water, % vol</td>
</tr>
<tr>
<td>Glycerol, % vol</td>
</tr>
<tr>
<td>PC, % vol</td>
</tr>
<tr>
<td>NaCl, % vol</td>
</tr>
<tr>
<td>Polymer A, % wt</td>
</tr>
<tr>
<td>Polymer B, % wt</td>
</tr>
<tr>
<td>Alddehyde, ppm</td>
</tr>
<tr>
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</tr>
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</tr>
</tbody>
</table>

3Fluids gelled, off-scale measurement.

[0048] Thermal conductivity measurements: The importance of a low thermal conductivity (K) is an important aspect of the success of insulating fluids. For effective reduction of
heat transfer, aqueous-based packer fluids in the density range of 8.5 to 12.3 ppg are expected to exhibit values for K of 0.3 to 0.2 BTU/hr ft °F, and preferably would have lower values. From the various formulations listed above, using these formulations fluid densities of 8.5 to 14.4 ppg were observed, all of which have a thermal conductivity of <0.2 BTU/hr ft °F as shown in Tables 1 and 2.

Example 2

We studied the formulation and testing of various combinations of inorganic, organic, clay and polymeric materials for use as viscosifying/gelling agents in aqueous based fluids for insulating fluids. We conducted a series of tests in which the solubility, thermal conductivity, thermal stability, pH, gelling properties, Rheological behavior, and toxicity of the various fluids were evaluated and compared. Perhaps most importantly, the thermal stability ranges from 37 °F to 500 °F and above were evaluated. These tests were conducted over short and long term periods. FIG. 3 lists the materials used in the formulations and the amounts tested. This in no way should be construed as an exhaustive example with reference to the invention or as a definition of the invention in any way.

Thermal stability and static aging: All formulations of fluids were statically aged at temperatures about 400 °F. for 3 day intervals. Formulations and properties for the tested fluids are shown in Tables 3 and 4 below. Most of the fluids appeared to remain intact, with the crosslinked systems showing an increase in viscosity and what appeared to be complete gelation behavior. We believe that these systems appeared to exhibit more desirable stability properties than other fluids, which included numerous biopolymers (e.g., xanthan, welan, and diutan gums) and inorganic clays and were generally destroyed after 3 days at 250 °F. In addition, as to the thermal stability of these formulations tested, less than 1% syneresis was observed for any of the samples.

| TABLE 4-continued
IPF Formulations and Properties After 72 Hours Static Aging at 450 °F. |
| Sample | 1 | 2 |
| Fann ® 35 Viscometer, 150 °F. | 130 °F. | 150 °F. |
| 600 rpm | 163 | 159 |
| 300 rpm | 127 | 122 |
| 200 rpm | 111 | 104 |
| 100 rpm | 82 | 86 |
| 6 rpm | 40 | 41 |
| 3 rpm | 36 | 37 |
| PV | 36 | 35 |
| YP | 91 | 85 |

Thermal conductivity measurements: The importance of a low thermal conductivity (K) is an important aspect of the success of insulating fluids. For effective reduction of heat transfer, aqueous-based packer fluids in the density range of 8.5 to 10.5 ppg are expected to exhibit values for K of 0.3 to 0.2 BTU/hr ft °F, and preferably would have lower values. From the various formulations listed above, using these formulations fluid densities of 8.5 to 10.5 ppg were observed, all of which have a thermal conductivity of <0.2 BTU/hr ft °F as shown in Tables 3 and 4.

Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. 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 and spirit of the present invention. All numbers and ranges disclosed above may vary by any amount (e.g., 1 percent, 2 percent, 5 percent, or, sometimes, 10 to 20 percent). Whenever a numerical range, R, with a lower limit, RL, and an upper limit, RU, is disclosed, any number falling within the range is specifically disclosed. In particular, the following numbers within the range are specifically disclosed: R=RL+k% (RU−RL), wherein k is a variable ranging from 1 percent to 100 percent with a 1 percent increment, i.e., k is 1 percent, 2 percent, 3 percent, 4 percent, 5 percent, 6 percent, 7 percent, 8 percent, 9 percent, 10 percent. Moreover, any numerical range defined by two R numbers as defined in the above is also specifically disclosed. Moreover, the indefinite articles “a” or “an”, as used in the claims, are defined herein to mean one or more than one of the element that it introduces. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee.

What is claimed is:

1. A method comprising:

providing an annulus between a first tubing and a second tubing;
providing an aqueous-based insulating fluid that comprises an aqueous base fluid, a water-miscible organic liquid, and a layered silicate; and
placing the aqueous-based insulating fluid in the annulus.

2. The method of claim 1 wherein the aqueous-based insulating fluid further comprises a polymer.

3. The method of claim 1 wherein the aqueous-based insulating fluid further comprises at least one additive selected from the group consisting of: a corrosion inhibitor, a pH modifier, a biocide, a glass bead, a hollow sphere, a hollow microsphere, a rheology modifier, a buffer, a hydrate inhibitor, a breaker, a tracer, an additional weighting agent, a viscosity modifier, and a surfactant.

4. The method of claim 1 wherein the aqueous base fluid comprises at least one brine selected from the group consisting of: NaCl, NaBr, KCl, CaCl₂, CaBr₂, ZrBr₂, sodium carbonate, sodium formate, potassium formate, cesium formate, and a derivative thereof.

5. The method of claim 1 wherein the water-miscible organic liquid comprises at least one liquid selected from the group consisting of: an ester, an amine, an alcohol, a polyol, a glycol ether, and a derivative thereof.

6. The method of claim 5 wherein the polyol comprises at least one polyol selected from the group consisting of: a water-soluble diol; ethylene glycol; propylene glycol; polyethylene glycol; polypropylene glycol; diethylene glycol; triethylene glycol; dipropylene glycol; tripropylene glycol; a reaction product formed by reacting ethylene and propylene oxide with an active hydrogen base compound; a reaction product formed by reacting polyethylene glycol and polypropylene glycol with an active hydrogen base compound; neopentyl glycol; a pentanediol; butanediol; an unsaturated diol; a butyne diol; a butene diol; a triol; glycerol; an ethylene oxide adduct, a propylene oxide adduct; pentaerythritol; a sugar alcohol; and a derivative thereof.

7. The method of claim 1 wherein the layered silicate comprises at least one layered silicate selected from the group consisting of: smectite, vermiculite, swellable fluoromica, montmorillonite, beidellite, hectorite, and saponite.

8. The method of claim 7 wherein the layered silicate is a synthetic layered silicate.

9. The method of claim 7 wherein the layered silicate is present in the fluid in an amount in the range of from about 0.1% to about 15% by weight of the fluid.

10. The method of claim 7 wherein the water-miscible organic liquid is present in the fluid in an amount in the range of from about 40% to about 99% by weight of the fluid.

11. A method comprising:
providing an apparatus comprising a tubing that comprises a fluid located within a well bore such that an annulus is formed between the tubing and a surface of the well bore;
providing an aqueous-based insulating fluid that comprises an aqueous base fluid, a water-miscible organic liquid, and a layered silicate; and
placing the aqueous-based insulating fluid in the annulus.

12. The method of claim 11 wherein the aqueous-based insulating fluid further comprises a polymer.

13. The method of claim 11 wherein the aqueous base fluid comprises at least one brine selected from the group consisting of: NaCl, NaBr, KCl, CaCl₂, CaBr₂, ZrBr₂, sodium carbonate, sodium formate, potassium formate, cesium formate, and a derivative thereof.

14. The method of claim 11 wherein the water-miscible organic liquid comprises at least one liquid selected from the group consisting of: an ester, an amine, an alcohol, a polyol, a glycol ether, and a derivative thereof.

15. The method of claim 14 wherein the polyol comprises at least one polyol selected from the group consisting of: a water-soluble diol; ethylene glycol; propylene glycol; polyethylene glycol; polypropylene glycol; diethylene glycol; triethylene glycol; dipropylene glycol; tripropylene glycol; a reaction product formed by reacting ethylene and propylene oxide with an active hydrogen base compound; a reaction product formed by reacting polyethylene glycol and polypropylene glycol with an active hydrogen base compound; neopentyl glycol; a pentanediol; butanediol; an unsaturated diol; a butyne diol; a butene diol; a triol; glycerol; an ethylene oxide adduct, a propylene oxide adduct; pentaerythritol; a sugar alcohol; and a derivative thereof.

16. The method of claim 11 wherein the layered silicate comprises at least one layered silicate selected from the group consisting of: smectite, vermiculite, swellable fluoromica, montmorillonite, beidellite, hectorite, and saponite.

17. The method of claim 12 wherein the layered silicate is a synthetic layered silicate.

18. A method comprising:
providing a first tubing that comprises at least a portion of a pipeline that contains a first fluid;
providing a second tubing that substantially surrounds the first tubing thus creating an annulus between the first tubing and the second tubing;
providing an aqueous-based insulating fluid that comprises an aqueous base fluid, a water-miscible organic liquid, and a layered silicate; and
placing the aqueous-based insulating fluid in the annulus.

19. The method of claim 18 wherein the aqueous-based insulating fluid further comprises a polymer.

20. The method of claim 18 wherein the layered silicate comprises at least one layered silicate selected from the group consisting of: smectite, vermiculite, swellable fluoromica, montmorillonite, beidellite, hectorite, and saponite.

21. The method of claim 18 wherein the water-miscible organic liquid comprises at least one liquid selected from the group consisting of: an ester, an amine, an alcohol, a glycol ether, and a derivative thereof.

22. The method of claim 21 wherein the polyol comprises at least one polyol selected from the group consisting of: a water-soluble diol; ethylene glycol; propylene glycol; polyethylene glycol; polypropylene glycol; diethylene glycol; triethylene glycol; dipropylene glycol; tripropylene glycol; a reaction product formed by reacting ethylene and propylene oxide with an active hydrogen base compound; a reaction product formed by reacting polyethylene glycol and polypropylene glycol with an active hydrogen base compound; neopentyl glycol; a pentanediol; butanediol; an unsaturated diol; a butyne diol; a butene diol; a triol; glycerol; an ethylene oxide adduct, a propylene oxide adduct; pentaerythritol; a sugar alcohol; and a derivative thereof.

23. The method of claim 18 wherein the layered silicate is present in the fluid in an amount in the range of from about 0.1% to about 15% by weight of the fluid and the water-miscible organic liquid is present in the fluid in an amount in the range of from about 40% to about 99% by weight of the fluid.

24. An aqueous-based insulating fluid comprising:
an aqueous base fluid,
a water-miscible organic liquid, and
a layered silicate.

* * * * *