Disclosed is a method of reducing lost circulation, sealing lost circulation zones, and stabilizing weak formations, using copolymers of ethylene acryl or ethylene methacrylic acid, or the single valence ionomers thereof, characterized as low density, solid at ambient temperature, reactive in selected temperature ranges, ductile, and able to adhere to rock and to each other to form ionomers in situ, wherein said copolymers are optionally used in combination with other solid agents, and wherein the treatment of said zones can be further enhanced by particle sizing and by blending into the treatment mixture multivalent alkaline earth and/or transition metals to provide optimum properties for the resulting ionomers given formation temperatures, conditions, and compositions.
METHOD FOR SEALING LOST CIRCULATION ZONES

FIELD OF THE INVENTION

[0001] This invention is related to a method of sealing lost circulation zones in a wellbore or stabilizing weak formations. More particularly, this invention relates to a method of addressing lost circulation problems employing a treatment mixture containing one or more copolymers of ethylene acrylic acid or ethylene methacrylic acid copolymer(s), or the single valence ionomers thereof, that are characterized by low density, reactivity, deformability, and the ability to react with other solids and the rock of exposed formations to provide a flexible, resilient sealing material. The copolymers improve adhesion to rock surfaces and consolidate individual solids into a cohesive mass that effectively seals the lost zone. The invention also relates to enhancing the performance of the copolymers by: 1) blending into the treatment mixture one or more divalent or multivalent alkaline earth or transition metal ions chosen for specific formation temperatures, conditions, and composition in order to control the ionomer formed in place; and 2) sizing and mixing particles.

BACKGROUND OF THE INVENTION

[0002] Rotary drilling of a borehole is accomplished by rotating a normally hollow drill string having a drill bit at its lower end. Weight is applied to the drill string while rotating to create a borehole into the earth. The borehole may pass through numerous different strata before the borehole reaches the desired depth. Sections are added to the drill string to increase its length as the borehole is deepened.

[0003] This drilling process creates significant amounts of friction that produces heat along with fragments of the strata being penetrated. The fragments of strata must be removed from the borehole and the drill bit must be cooled to extend its usable life. The circulation of a drilling fluid down through the drill string and up the annulus between the drill string and borehole wall to the surface accomplishes both of these requirements. Cooling of the drill bit is accomplished by a steady flow of cool fluid from the surface and cutting fragments are carried up the annulus to the surface where they are separated from the drilling fluid. The drilling fluid is usually treated and reused.

[0004] Drilling fluids typically include water and complex mixtures of clays, polymeric thickeners, dispersants, and weighting agents. The properties of the drilling fluid are dictated primarily by the physical nature of the geological formation through which the borehole will be created. The hardness, fluid content, type of fluid, porosity, permeability, in-situ stresses, compressive and tensile strength, and chemical composition are all important characteristics of a geological formation which impact the formulation of the drilling fluid.

[0005] In addition to providing cooling, lubrication, and cuttings removal from the borehole, the drilling fluid also provides pressure control for the well. The column of drilling fluid in the borehole produces a hydrostatic pressure. The density of the drilling fluid may be varied to produce a hydrostatic pressure at specific points along the borehole that is equivalent to or slightly in excess of the pressure of the exposed geologic formations. However, such pressure may be compromised or lost when the drill bit encounters certain unfavorable subterranean zones, which may comprise, for example, comparatively low-pressure zones, such as vugs, fractures, and other thief zones. Similarly, encountering comparatively high pressure subterranean zones results in crossflows or underground blowouts. In some cases, the hydrostatic pressure of the drilling fluid column that is required to control a formation pressure in part of the borehole might exceed the tensile or compressive strength of other exposed formations. If this happens, a fracture may be initiated and propagated in the weaker strata. This also causes an alteration in the drilling fluid circulation circuit. Instead of returning to the surface up the annulus, some or all of the drilling fluid will exit the borehole through the created fracture or fractures. These situations are commonly referred to in drilling practice as “lost circulation”. Lost circulation is the loss of fluids from the wellbore to exposed formation. Fluid exiting the wellbore may enter the porosity/permeability of formations, vugs, natural fractures, induced fractures, or similar cavities present or created in the formation. Lost circulation is one of the most common borehole stability problems in drilling/workover operations worldwide. Lost circulation costs the industry approximately $500 million annually. In all cases, it is important to the drilling process to restore the circulation back to the surface within the borehole.

[0006] A further complication is that some of these zones that permit the influx of water from the water-bearing zones may reduce the amount of hydrocarbons that can be recovered from the well, and might require additional separation and disposal procedures if the water is removed from the well along with oil and gas. Thus, it is beneficial to limit the flow from water-bearing regions so that the desired oil or gas can be recovered more efficiently.

[0007] One approach for sealing zones to remedy lost circulation is to add materials known as bridging additives to the drilling fluid materials to block the leak path of the exiting fluid. Bridging materials may include, for example, cottonseed hulls, ground mica, graded sand, walnut or other nut hulls ground to different sizes, diatomaceous earth, gilsonite, ground coal, charcoal, cellophane flakes, and shredded paper. These materials are not deformable and are simply held in place by differential pressure. These materials only bridge or plug and do not form a high strength solid material to seal the leak path. Another approach utilizes ground rubber tires or shaped plastic pellets. These latter materials may be deformable, but have no adhesive properties.

[0008] Another method of sealing zones to remedy lost circulation is to use cement compositions, but they are often unacceptable due to relatively slow setting time. Portland cement mixtures are often used to provide a more permanent seal. One of the limitations of Portland cement formulations is susceptibility to drilling fluid contamination. Contamination of the cement slurry with drilling fluid often reduces the compressive strength of the set cement, may greatly extend the setting time of the slurry, and may affect the bonding of the cement to the formation. This is particularly true if the drilling fluid contains significant concentrations of lignosulfonate thickeners, carboxylate-hydroxide polymers such as starch, hydroxyethyl cellulose, carboxymethyl cellulose, carboxymethyl hydroxyethyl cellulose, or polyalcohols.
Another limitation of Portland cement mixtures is density. As discussed above, the cause of the lost circulation problem may be use of too heavy mud, which causes fracture initiation or propagation in strata surrounding the borehole. Portland cement mixtures are relatively dense and may simply aggravate this problem. Diluting the Portland cement to reduce its density is not an acceptable solution to this problem since the dilution weakens the Portland cement (i.e. Portland cement is very sensitive to its water/cement ratio).

U.S. Pat. No. 5,325,922, incorporated by reference herein in the entirety, discloses a method for restoring drilling fluid circulation to a borehole of a well comprising circulating a non-conventional cementious slurry such as drilling fluid-blast furnace slag mixture into the strata, and allowing the mixture to solidify in situ. This slurry does not have the disadvantage of Portland cement of being affected by the drilling fluid or brine.

Compositions that set faster exist. Some are mixtures of clay and aqueous rubber latex or hydratable polymers. (See, for example, U.S. Pat. Nos. 5,913,364; 6,060,434; 6,167,967; and 6,258,757).

It is also known to modify the properties of a subterranean strata penetrated by a wellbore using hardenable epoxy resins. For example, U.S. Pat. No. 5,873,413 discloses pumping an epoxide-containing liquid and a hardening agent into a subterranean stratum by way of the wellbore and allowing the composition to harden in the stratum. This requires an extra component, the hardening agent, and the result is a thermoset composition.

Copolymers of ethylene and acrylic acid or methacrylic acid, and the neutralized or partially neutralized salts, or ionomers thereof, are known in the art relating to thermoplastics, particularly in applications for packaging, automotive seals, footwear, gaskets, hoses, coatings, and golf balls, but no references have been found suggesting the use of said copolymers in an application in a subterranean formation.

There are numerous treatments available in the art for addressing the permeability/porosity of formations. There are few treatments that are broadly applicable and highly effective for severe to total lost circulation. This is particularly true for losses to vugular or fractured formations.

There is a need in the art for a method of treating lost circulation that provides a flexible, resilient sealing material that permits improved adhesion to rock surfaces and that consolidates the individual solids into a cohesive mass that effectively seals the lost zone, whether the zone is typified by severe losses such as vugulars or fractures, or whether the formation is cracked and brittle and needs to be reinforced and strengthened.

If such a treatment were available, it would be a distinct advantage if it were possible to further enhance the treatment and tailor the ionomers formed in the resulting solid mass for specific temperatures, conditions, and formation composition.

It would also be advantageous if the treatment materials were low density so that the hydrostatic pressure of the treatment fluid would not worsen problems associated with fracture initiation, as is often the case with cement formulations.

Finally, it would be a distinct advantage if the treatment could be formulated with either water-based or non-aqueous based wellbore fluids.

Accordingly, the present invention is directed to overcoming the above noted problems in the art and demonstrates the noted advantages.

SUMMARY OF THE INVENTION

In accordance with the foregoing the present invention is a method of treating a subterranean zone penetrated by a wellbore, said zone characterized by lost circulation, employing materials characterized by low density, reactivity, deformability, and the ability to adhere/ bond to rock formations and each other to form a cohesive mass in situ to seal lost circulation zones and/or stabilize weak formations, said method comprising:

a) Placing one or more copolymers of ethylene acrylic and ethylene methacrylic acid, or the single valence ionomers thereof, that react in a selected temperature range, optionally in combination with other solid agents, in a drilling fluid treatment mixture and circulating in the wellbore in the zone of lost circulation;

b) Temporarily discontinuing circulation of fluid in the wellbore; and

c) Allowing the wellbore to remain static for a period of time sufficient to cause an increase in the temperature of the wellbore;

d) Thereby causing said copolymer(s) to melt and react with the formation and any other solids in the treatment, thus forming a cohesive mass that adheres to the formation surfaces of the loss zone.

In a related embodiment the method comprises:

a) Placing one or more copolymers of ethylene acrylic and ethylene methacrylic acid, or the single valence ionomers thereof, that react in a selected temperature range, optionally in combination with other solid agents, in a drilling fluid treatment mixture and injecting the treatment mixture into a natural fissure or fracture, induced fissure or fracture, vug, fault or other opening existing in the zone of lost circulation;

b) Temporarily discontinuing injection of fluid in the wellbore;

c) Allowing the wellbore to remain static for a period of time sufficient to cause an increase in the temperature of the wellbore, fracture, fissure, vug or fault;

d) Thereby causing said copolymer(s) to melt and react with the formation and any other solids in the treatment, thus forming a cohesive mass that adheres to the formation surfaces of the loss zone.

In another embodiment the invention is also the blending into the treatment mixture of divalent or multivalent alkaline earth and/or transition metal ions to provide
optimum properties in the ionomers formed in situ for specific formation temperatures, conditions, and compositions.

[0031] In yet another embodiment the invention is a drilling fluid composition, which can be water-based or non-aqueous based, containing in the range of 5 to 100 lbs/barrel copolymer selected from ethylene acrylic acid and ethylene methacrylic acid, or the single valence ionomers thereof, individually or in combination, added as solid particles selected from one or more sizes, and further optionally containing a divalent or multivalent ion selected from the group consisting of alkaline earth metal ions and transition metal ions, and further optionally containing other solid agents known in the art, selected from bridgers, fillers, surface pluggers, and interstitial pluggers.

BRIEF DESCRIPTION OF THE DRAWINGS

[0032] FIG. 1a is a drawing of the equipment used in the slot test.

[0033] FIG. 1b is a drawing of the equipment used in the slot test in the inverted position where the seal is tested.

DETAILED DESCRIPTION OF THE INVENTION

[0034] In the present invention one or more copolymer(s) of ethylene acrylic or ethylene methacrylic acid, or the single valence metal salt ionomers thereof, are reacted with other solid agents and the rock of exposed formations to provide flexible, resilient sealing material. Copolymers of ethylene acrylic acid and ethylene methacrylic acid are subject to crosslinking with divalent or multivalent ions and provide good adhesion to a variety of compositions in rock formations, including, but not limited to silica, alumina, shale, calcium, sodium, etc. The copolymers improve adhesion to rock surfaces and consolidate individual solids. Adhesion herein is defined as the attraction between dissimilar surfaces for one another, or the state in which two surfaces are held together by interfacial forces which may consist of valence forces, interlocking action, or both.

[0035] The copolymers and ionomers of the invention are low density so they do not unnecessarily increase the hydrostatic pressure of the treatment fluid. The materials are thermoplastic and heat activated and do not require additional hardening agents as with epoxies. The copolymers are placed at the circulating temperature of the wellbore into the loss zone. After treatment is placed the wellbore is allowed to remain static with no circulation, or loss of fluid sufficient to cool the wellbore, whereby increasing the temperature of the wellbore. As the temperature increases, the copolymers melt and react with the formation and other solids in the treatment. Adhesive three-dimensional mass is formed and adheres to the formation surfaces of the loss zone.

[0036] Copolymers that are useful in the present invention include copolymers of ethylene acrylic acid and ethylene methacrylic acid (Hereinafter referred to as EAA and EMA), individually or a combination thereof. Commericially such copolymers typically contain at least about 4% by weight, and up to about 25 weight percent acid content. The ethylene acrylic acid polymer structure is characterized by a greatly enhanced “molecular backbone” and side chains of acrylic acid. The carboxyl groups are free to form bonds and to interact with any polar substrate such as metals, glass, celluloses, and polyamides. Carboxyl groups on adjacent chains can hydrogen bond with each other. This permits a level of toughness not obtainable with other polymers. The polymer can be cross-linked through the backbone and the acid functionality, to provide additional improvements in toughness. The bulky carboxyl groups inhibit the ability of the polymer to crystallize, which improves optical clarity and reduces both melting and softening points. Typically, acid numbers denoting the number of COOH groups available identifies ethylene acrylic acid (EAA) and ethylene methacrylic acid (EMA). These acid numbers range from about 20 to 180, where the lower acid number resins generally provide a harder product and the higher numbers generally result in a softer product. Ethylene acrylic acid is available commercially as Primacor®, in a number of different formulations, from Dow Chemical Company. Ethylene methacrylic acid is available from DuPont Company under the tradename Nucrel®. Ethylene acrylic acid is available from Honeywell International, Inc. under the tradename A-C®.

[0037] As mentioned above, single valence metal salt ionomers of the copolymers of ethylene acrylic or methacrylic acid are also useful in the present invention. By ionomer is meant organometal compositions having a metal attached to or interlocking (crosslinking) a polymer chain. Ionomers are prepared by neutralization of the carboxyl acid group of the copolymers, or partial neutralization with metal ions. Fully neutralized EAA and EMA copolymers are known to have intractable melts. Multivalent ionomers are also considerably more viscous than their copolymer precursors. Therefore, fully neutralized ionomers generally have separate utility and significantly different properties from the non-neutralized ethylene/acid-copolymer base resins. Single valence ionomers, however, are useful in the present invention because the single valence species can be easily displaced by a multi-valent ion. Single valence ionomers include those formed by reaction of the acidic groups on the copolymer with alkaline salts of sodium, potassium, and lithium, or ammonia/ammonium (NH₄⁺/NH₃⁺). The acid groups can be completely or partially neutralized with the single valence metal or complex. In the present invention, non-neutralized copolymers, or partially neutralized single valence ionomers are preferred so that they can be reacted with mono-, di-, and multivalent ions downhole to create ionomers in place having desired properties to seal lost circulation zones. A suitable ionomer, containing sodium, is available commercially under the tradename AClyn®245 from Honeywell International, Inc. Other AClyn® ionomers contain zinc, calcium, and magnesium. Single valent ionomers containing sodium, as well as zinc ionomers, are available commercially under the tradename LOTEK from Exxon Mobil.

[0038] In the present invention the EAA and EMA copolymers and/or single valence ionomers can be used individually or in combination with other solid agents known in the art to bridge or plug lost circulation zones. Suitable solid agents include, bridging materials, such as, for example, ground mica, mica flakes, silica slag, hydrated borate, graded sand, diatomaceous earth, gisborne, ground coal, charcoal, cellophane flakes or strips, cellulose fiber, expanded perlite, shredded paper or paper pulp, and the like. Other solid agents include walnut or other nut hulls ground to different sizes, cottonseed hulls or cottonseed hulls, sugar
cane fibers or bagasse, flax, straw, ground hemp, ground fir bark, ground redwood bark and fibers, and grape extraction residue. Additional suitable materials include, for example, crystalline silicas, amorphous silicas, clays, calcium carbonate, and barite. Suitable amounts of additional solid agents for use in combination with the copolymer/s and/or ionomer(s) would be apparent to those skilled in the art. Since the copolymers are available in a variety of particle sizes the copolymer solid particles can also be used as lost circulation bridging materials.

[0039] The detection of lost circulation will generally occur in two ways, i.e. either circulation of the drilling fluid will stop, indicating total loss of the drilling fluid somewhere in the borehole, or a reduced rate of circulation of the drilling fluid through the borehole will be noted, i.e. more drilling fluid is being put in than is being taken out. The type or extent of lost circulation will dictate, to some degree, the response in correcting the lost circulation. Total loss of circulation or substantial loss of circulation will require the injection of more copolymer. As an example, where the loss is due to whole fluid loss into the matrix permeability of a geologic formation, a loss rate on the order of 1-10% of the circulating fluid might be typical. This would produce a loss rate of up to one barrel/minute for every ten barrels of fluid circulated in the wellbore. If the loss is due to a small crack or fissure, a loss on the order of 10 to 30% of the circulating fluid might be typical. This would amount to a loss in circulation of approximately one to three barrels/minute for every ten barrels of fluid circulated in the wellbore. Where the loss is due to, for example, a fracture where there is more capacity for the fluid to flow in, the lost volume might be in the range of 30-60% of the circulating fluid. Where the loss is due to a larger fracture or vugs, which may have an opening size of 0.15 inch or more wide for fractures and vugs with a diameter greater than about 0.125 inch and may extend a few feet to hundreds of feet from the wellbore, fluid lost could easily be much greater than 50-60% of the circulating volume.

[0040] In the present invention the EAA and EMA copolymers, and optionally other solid agents, are premixed and added to the drilling fluid. They can also be added to remedial fluid. The invention can be employed in either mitigation or remediation. Amounts required would be apparent to those skilled in the art, depending on the size of the loss zone, temperature and other conditions, and composition of the formation. A suitable amount would be in the range of from about 5-100 lbs/barrel of fluid, more often in the range of 10 to 50 lbs/barrel of fluid.

[0041] EAA and EMA copolymers are available in a variety of shapes and sizes, including, but not limited to prills, pellets, beads, granules, and powders. Proper sizing of the EAA and/or EMA copolymers and/or ionomers further aids bridging of the leak path. The particle sizes can be mixed to form a “lost circulation pill”. Also, sizes can be selected for particular conditions and the treating fluid may contain a mix of sizes for enhanced performance, as will be further discussed below.

[0042] In some applications of the present invention it is advantageous to utilize the copolymers in the form of a liquid dispersion. Liquid dispersions can also be used in the treatment mixture for suspension, variation of reactivity over a range of temperatures, and for small bridging particles. Heating up the copolymers and dropping them into solvent under high shear produces dispersions. This has the effect of increasing the copolymer surface area by breaking up the copolymer and forming vast numbers of smaller particles, each having readily available reactive groups. The use of dispersions can provide fast reaction times because more —COOH groups are exposed. The particles in dispersion may be in the range of 0.3 microns to 0.03 microns. Suitable ethylene acrylic acid dispersions are available commercially under the tradename Michem® Prime 4983R, 4983-40R, and 4990R from Michelman, Inc.

[0043] Non-aqueous dispersions or solutions of the polymers may also be made for application in the invention. Various solvents are employed or blends of solvents are used to dissolve both parts of the copolymer—the non-polar ethylene portion and the highly polar acid portion.

[0044] The EAA and/or EMA copolymers, and optionally other solid agents, can be incorporated into water-based drilling fluid formulations or non-aqueous or oil-based drilling fluid formulations. The term water-based fluid is intended to encompass both fresh water muds, salt water containing muds, whether made from seawater or brine, and other muds having water as the continuous phase including oil-in-water emulsions. In any event drilling fluid will always contain at least one additive such as viscosifiers, thinners, dissolved salts, solids from the drilled formations, solid weighting agents to increase the fluid density, formation stabilizers to inhibit deleterious interaction between the drilling fluid and geologic formations, and additives to improve the lubricity of the drilling fluid.

[0045] It is generally preferred that the water-based drilling fluids use water containing dissolved salts, particularly sodium chloride. In these instances, 0 to up to saturation, preferably 0.5 to 20, more preferably 0.2 to 5 wt % sodium chloride may be used. One suitable source to use is seawater or a brine solution simulating seawater. Various salts, preferably organic salts, are suitable for use in the drilling fluid used in this invention in addition to, or instead of NaCl, including, but not limited to, NaBr, KCl, CaCl₂, NaNO₃, Na₂CO₃, K₂CO₃, Na₂S, and K₂SO₄, among which sodium chloride is preferred, as noted above.

[0046] The term “oil-based fluids” is meant to include fluids having oil as the continuous phase, including low water content oil-base mud and invert oil-emulsion mud.

[0047] In the method of the present invention the described treating fluid is pumped to or into the zone of lost circulation or the fracture, and then the pumps are stopped. Then the wellbore is allowed to remain static and circulation of fluid to cool the wellbore/formation is temporarily halted, thereby causing an increase in the temperature of the wellbore. As the temperature increases, the EAA and/or EMA copolymer(s), and/or ionomer(s), individually or in combination, melt and react with the formation and other solids in the treatment. A cohesive mass is formed which adheres to the formation surfaces of the loss zone. Where the formation is cracked or brittle, the treatment holds loose material together. The materials used in the present method are deformable and adhesive. The copolymers are able to enter zones of lost circulation and react with divalent and multivalent ions to form a solid, three-dimensional mass that actually adheres to the walls of the formation and is essentially part of the structure. Accordingly, setting the copoly-
mer plug across the thief zone restores the loss of drilling fluid circulation while drilling.

[0048] In the case of a fracture, the treating fluid is pumped to the zone of the fracture and the pumping causes the fracture to open. The pumping is stopped. The treatment fluid containing copolymer(s) enters the zone, deforms, squeezes viscous material outward, and deposits at the point of the fracture farthest from the wellbore. When pumping is started back up the fracture is decreased in size and the viscous mass formed at the top (end farthest from the wellbore) provides substantial resistance to flow. Subsequently, when the well is pressured up again, it takes more pressure to open the fracture, fluid loss is reduced, and the fracture doesn’t extend. The fracture may balloon or swell, but generally does not grow.

[0049] Performance of the treating fluid of the present invention can be further enhanced. One method is by adding a source of divalent or multivalent ion such that when the EAA and/or EMA copolymer(s) react downhole it is possible to control properties of the copolymer(s) and solid mass formed in situ. The treatment is also enhanced by particle sizing and by selecting acid numbers suitable for particular temperatures.

[0050] By adding a source of divalent or multivalent alkaline earth or transition metal ion to the treating fluid, said ions are available when the reaction takes place and it is possible to control the final properties of the ionomer that will result and tailor it to wellbore conditions. Even if an ion is supplied that controls formation of the resulting ionomer, there are still other unreacted groups on the copolymer(s) that can adhere/bond to the rock, forming an extensive solid cohesive mass that connects all the surfaces. Suitable divalent and multivalent ions are selected from alkaline earth metals and transition metals. Specific examples would include, but not be limited to ZnO, MgO, CaCO₃, Zn(OH)₂, Zn(CO₃)₂, and lime. Suitable ions could be part of the treating fluid mixture or could possibly be added as smaller particles or powders.

[0051] As mentioned selected sizing of the copolymers further aids bridging of the leak path. The EAA and/or EMA copolymers are available in a variety of sizes including pellets, prills, powders, dispersions, etc. It is possible to select a mix of particle sizes that permits the mixture of particles to exhibit the properties of a slurry with additional benefits in situ. Sizing of bridging particles for lost circulation treatments is generally well known by those skilled in the art. Typically, a substantial portion of the solids have an effective width or diameter approximately equivalent to ½ to ½ the width or diameter of the opening to be sealed (fracture, fissure, vug or fault). The size of the largest particles and the volumetric amount in the treatment volume can be used to effectively size and determine the volumetric fraction of each additional particle used in the treatment. Packing of the largest particles creates a natural porosity in the treatment fluid. The next size particle is selected to fit in the porosity created by the large particles without disrupting the packing configuration. Additional porosity exists in the pack created by the two particle sizes. Smaller particles can be added to fill in the remaining spaces in the particle pack again without disrupting the packing configuration. Usually 2 to 4 particle sizes are added and more commonly 2 to 5 particle sizes are added to create this optimum blend ratio (by size and volumetric fraction) within the treatment. Fine solids in the drilling fluid can fill remaining porosity in the dispersion of solid particles within the treatment. Generally in a slurry of solids and liquids such as drilling fluids and cement slurries the solids may make up about 10-50% of the volume with the remaining volume comprising a liquid such as oil, water, an emulsion of water in oil or an emulsion of oil in water, brine, the liquid being necessary for adjusting viscosity. By sizing large particles to occupy the most volume possible and filling in with smaller solids up to 90%, even 90% of the volume can comprise solids and leave enough volume for only about 10-20% liquid. Such a mixture will pour like a slurry, however if this mixture of 80-90% solids loses a small amount of liquid, even 1% volume of liquid, it will no longer flow. It has surprisingly been found that this has a very beneficial application in treating lost circulation zones, because with the differential pressure across the wellbore, as the mixture arrives at the loss zone, it has a tendency to flow in a little, lose some fluid by filtration and then become unflowable. Refractable castable cements and ceramics industries utilize this particle sizing technology. A reference explaining the design of such optimum packing of bridging slurries is the book “Predictive Process Control of Crowded Particulate Suspensions” by James E. Funk and Dennis R. Dinger (Kluwer Academic Publishers, Boston, ISBN No. 0-7923-9409-7, 1994, second printing 1997).

[0052] EAA and EMA copolymers should be selected with regard for the optimum acid number for the temperatures to be encountered in the well. Acid numbers indicate the number of —COOH groups available, and for ethylene/ acrylic copolymers acid numbers range from about 20 to 180, where the lower numbers generally react to form harder materials and the higher numbers react to form softer materials. Temperatures in the wellbore may be in the range of 65°C to 150°C, more often from about 85°C to 120°C. Typically acid numbers of 20 to 80 provide more desirable results in temperatures in the range of about 85°C to 120°C. Where the temperature is less than 65°C acid numbers in the range of 120-180 were more useful.

[0053] In the present invention various formulations were evaluated using a slot test method to find whether they could successfully deform, adhere, and plug large fractures having lost circulation. This is demonstrated in Examples 6 through 9. The equipment used in the slot test method is shown in FIG. 1a. Before the test starts the temperature is increased to the target temperature and held there for 60 minutes. It is important to obtain at least a 1000 psi differential across the slot. With reference to FIG. 1a, there is a slot 5 where the seal is tested. The slot is driven by a motor 9 and the whole assembly, including the heat jacket around the slot 5. Also shown is a mixing vessel 1 equipped with a mixing paddle 8 and surrounded by a heat jacket 6. Also shown is a slot 5 where the seal is tested. The mixing vessel is a receiving vessel 2, which receives the mixture, when the vessels are inverted at the point where the seal is tested. FIG. 1b shows the equipment in the inverted position. When the equipment is inverted the 1000 psi differential drives the mixture through the slot. A device (not shown) measures how much fluid comes through. The receiving vessel includes a drain hole 3. Between the two vessels is a valve 4. In a successful test the material will pack off and the flow will stop completely.

[0054] In the tests slot openings ranged in width from 0.02 inches to 0.1 inches. Many conventional lost circulation
materials will bridge slots of 0.02 inches. Few lost circulation materials can be formulated to completely bridge and seal slot widths of 0.04 inches. Slot widths, corresponding to fracture widths >0.04 inches are extremely difficult to seal with non-reactive, non-deformable materials. For a successful test, the slot has to react and adhere enough that it completely bridges off, or packs and sticks. Two other possible outcomes of the slot test are: 1) The solid particles don’t deform, just pack in the vicinity of the seal, permitting flow paths through the particles and eventually leaks; 2) The solid particles plastically deform and fill the seal and there are no holes, but they are above softening point, which is separate from melting point, and may differ by 15-20 or 30° F. (8-11 or 17° C.).

[0055] The following examples will serve to illustrate the invention disclosed herein. The examples are intended only as a means of illustration and should not be construed as limiting the scope of the invention in any way. Those skilled in the art will recognize many variations that may be made without departing from the spirit of the disclosed invention.

EXAMPLE 1

[0056] To one barrel of diesel oil invert emulsion drilling fluid was added 20 lb/bbl Dow Primacor® 3460, 15 lb/bbl Allied Signal A-C 580, and 10 lb/bbl Allied Signal A-C 540A. The mixture was poured into a test vessel and the temperature increased to 100° C. to simulate the temperature in a wellbore. After 4 hours a highly viscous semi-solid mass formed that adhered to the test vessel wall. Portions of the material having larger particles, Dow Primacor® 3460, were dissolved with portions of the polymer bead softened and deformable with applied pressure.

EXAMPLE 2

[0057] In Example 2, to one barrel of synthetic oil invert emulsion drilling fluid was added 20 lb/bbl Dow Primacor® 3150 and 20 lb/bbl Allied Signal A-C 540A. The mixture was poured into a test vessel and the temperature increased to 120° C. to simulate the conditions in a wellbore. After 4 hours a viscous mass was formed.

EXAMPLE 3

[0058] To one barrel of synthetic oil invert emulsion drilling fluid was added 20 lb/bbl Allied Signal A-C 540A, 15 lb/bbl Allied Signal A-C 5120, 10 lb/bbl Allied Signal A-C 580, and 20 lb/bbl zinc oxide. The mixture was poured into a test vessel and the temperature increased to 105° C. to simulate conditions in a wellbore. After 4 hours a semi-solid, deformable mass was formed.

EXAMPLE 4

[0059] In Example 4 a water base mud and an aqueous dispersion of ethylene-acrylic acid copolymer was mixed in a volumetric ratio of 1:1. A viscous mass formed immediately upon mixing. The mixture was allowed to stand for 2 hours at a test temperature of 95° C. After 2 hours a semi-solid mass was formed that would not flow.

EXAMPLE 5

[0060] Example 4 was repeated, using a water base mud and an aqueous dispersion of ethylene-acrylic acid copolymer in a volumetric ratio of 1:1, but this time before mixing the water base drilling fluid with the copolymer dispersion, 20 lb/bbl of calcined magnesium oxide was added to the drilling fluid. Again a viscous mass formed immediately upon mixing. This time the mixture formed a plastic solid after 4 hours at 95° C.

Lost Circulation Tests

[0061] Examples 6 through 9 utilized the slot test method and employed the equipment shown in FIG. 1a and 1b, discussed above, to evaluate the efficiency of various materials to deform, adhere, and plug fractures. The slot employed for the test had a width of 0.04 inches. Slot widths, corresponding to fracture widths >0.04 inches are extremely difficult to seal with non-reactive, non-deformable materials.

EXAMPLE 6

[0062] In Example 6 the efficiency of these materials to deform, adhere, and plug large fractures was evaluated using the slot test method. To one barrel of diesel oil invert emulsion drilling fluid was added 15 lb/bbl Dow Primacor® 59901, 15 lb/bbl Allied Signal A-C 5120, and 15 lb/bbl Allied Signal A-C 540A. The mixture was placed into the slot tester and inverted so test solution was not in contact with the slot. A stirring paddle in the pressure vessel stirred the solution during heating to prevent settling. Pressure in the pressure vessel was increased to 1000 psi. The mixture was heated to a test temperature of 125° F. (52° C.) in 60 minutes and held at 125° F. (52° C.) for 60 minutes prior to conducting the sealing test. Pressure in the test chamber was increased to 1250 psi and pressure in the receiving vessel below the slot was increased to 250 psi to provide 1000 psi differential pressure for the test. After 2 hours elapsed time from the start of the test, the pressure vessel was rotated to allow the sample solution to contact the slot. A valve below the slot was opened to allow fluid flow through the slot into a receiving vessel. The result was that all of the test fluid flowed through the slot in less than 30 seconds.

EXAMPLE 7

[0063] In Example 7 the formulation and test procedure was exactly the same as in Example 6, except the test temperature was increased to 150° F. (66° C.). The result was that a partial seal was formed and then was destroyed, and all the test fluid flowed through the slot in approximately 45 seconds.

EXAMPLE 8

[0064] The formulation and test procedure of Example 8 was exactly the same as Example 6, except the test temperature was 175° F. (79° C.). The result was that a partial seal formed, but all the test fluid flowed through the slot in 3 minutes.

EXAMPLE 9

[0065] The formulation and test procedure of Example 9 was exactly the same as Example 6, except the test temperature was increased to 210° F. (95° C.). The result was that a seal was formed and held 1000 psi differential for 50 minutes.
1. A method of treating a borehole/wellbore penetrating a subterranean formation which comprises:

a) mixing one or more copolymers selected from ethylene acrylic acid, ethylene methacrylic acid, or any single valence ionomer of ethylene acrylic acid or ethylene methacrylic acid, individually or in combination, and optionally other solids and additives, in a wellbore fluid selected from drilling fluid and remedial fluid, and circulating in the wellbore;

b) temporarily discontinuing circulation of fluid in the wellbore; and

c) allowing the wellbore to remain static for a period of time sufficient to cause an increase in the temperature of the wellbore;

d) thereby causing said copolymer(s) or ionomer(s) thereof to melt and react with the formation and any other solids in the treatment, thus forming a cohesive mass that will adhere to the formation surfaces.

2. The method of claim 1 further comprising the method is utilized for one or more of the following:

- reducing lost circulation of drilling fluid; sealing lost circulation zones; sealing a natural fissure or fracture, induced fissure or fracture, vug, fault or other opening existing in the zone of lost circulation; and treating weak zones of the formation to increase stability.

3. The method of claim 1 further comprising the copolymers and/or ionomers are utilized as solid particles and the treatment method is enhanced by particle sizing.

4. The method of claim 1 further comprising the treatment method is enhanced by selecting acid numbers of the copolymers and/or ionomers for their properties at particular temperatures.

5. The method of claim 2 wherein the method is used to treat a zone of lost circulation further comprising:

a) circulating said copolymers and/or ionomers in the wellbore in the zone of lost circulation;

b) temporarily discontinuing circulation of fluid in the wellbore; and

c) allowing the wellbore to remain static for a period of time sufficient to cause an increase in the temperature of the wellbore;

d) thereby causing said copolymer(s) or ionomer(s) thereof to melt and react with the formation and any other solids in the treatment, thus forming a cohesive mass that will adhere to the formation surfaces in the zone of lost circulation.

6. The method of claim 2 wherein the method is utilized to seal a natural fissure or fracture, induced fissure or fracture, vug, fault or other opening existing in the zone of lost circulation further comprising:

a) injecting said treatment mixture into a natural fissure or fracture, induced fissure or fracture, vug, fault or other opening existing in the zone of lost circulation;

b) temporarily discontinuing injection of fluid in the wellbore; and

c) allowing the wellbore to remain static for a period of time sufficient to cause an increase in the temperature of the wellbore, fracture, fissure, vug or fault;

d) thereby causing said copolymer(s) to melt and react with the formation and any other solids in the treatment, thus forming a cohesive mass that adheres to the formation surfaces of the natural fissure or fracture, induced fissure or fracture, vug, fault or other opening existing in the zone of lost circulation.

7. The method of claim 2 wherein the method is utilized to strengthen a weak or unstable zone in the wellbore further comprising:

a) circulating said copolymers and/or ionomers in the wellbore in the zone of weakness or instability;

b) temporarily discontinuing circulation of fluid in the wellbore;

c) allowing the wellbore to remain static for a period of time sufficient to cause an increase in the temperature of the wellbore; and

d) thereby causing said copolymer(s) or ionomer(s) thereof to melt and react with the formation and any other solids in the treatment, thus forming a cohesive mass that will adhere to the formation surfaces in the zone of weakness or instability.

8. The method of claim 1 wherein the single valence ionomers are single valence metal salt ionomers.

9. The method of claim 8 wherein the single valence metal salt ionomers are selected from single valence ionomers formed by reaction of the acidic groups on the copolymer(s) with alkaline salts of sodium, potassium, and lithium, or ammonia/ammonium (NH₃/NH₄⁺).

10. The method of claim 4 wherein the copolymers have acid numbers in the range of about 20 to 180.

11. The method of claim 10 further comprising the wellbore has a temperature in the range of about 85°C to 120°C, and the copolymers employed have acid numbers in the range of 20 to 80.

12. The method of claim 10 further comprising the wellbore has a temperature in the range of less than 65°C, and the copolymers employed have acid numbers in the range of 120-180.

13. The method of claim 3 further comprising the copolymers and/or ionomers are added as solid particles of different sizes.

14. The method of claim 13 wherein the copolymers and/or ionomers are selected from the group consisting of pellets, prills, beads, granules, or powders.

15. The method of claim 3 further comprising the copolymers and/or ionomers are utilized in the treatment as a dispersion.

16. The method of claim 15 wherein the size of the particles in the dispersion are in the range of 0.3 microns to 0.03 microns.

17. The method of claim 13 further comprising a mix of different sizes of solid particles of copolymer is employed that further aids bridging of a leak path.

18. The method of claim 17 further comprising the particles are sized such that large particles take up the most volume possible and the remaining volume is filled in with smaller solids.

19. The method of claim 18 wherein large particles are sized to occupy the most volume possible and filled in with
smaller solids up to 80-90% of the volume, leaving enough volume for only 10-20% liquid by volume.

20. The method of claim 19 further comprising the particles are sized such that when the mixture enters a lost circulation zone, some fluid is lost, causing the remaining volume of large and smaller particles to lose flow properties and lock in place.

21. The method of claim 1 further comprising optionally adding at least one divalent or multivalent ion selected from the group consisting of alkaline earth metal ions and transition metal ions, or combinations thereof.

22. The method of claim 21 wherein the divalent or multivalent ions selected from the group consisting of alkaline earth metal ions and transition metal ions, or combinations thereof, are chosen for specific formation temperatures, conditions, and composition in order to control the ionomer(s) formed in place.

23. The method of claim 21 wherein the divalent or multivalent ion(s) is selected from the group consisting of ZnO, MgO, CaCO₃, Zn(OH)₂, Zn(CO₃)₂, and lime, and combinations thereof.

24. The method of claim 21 wherein the divalent or multivalent ion(s) can be utilized as part of the treating fluid or added as smaller particles or powders.

25. The method of claim 1 further comprising the treating fluid contains other solid agents selected from bridgers, fillers, surface plugging and interstitial agents, or a combination thereof.

26. The method of claim 1 further comprising the copolymer(s) and/or ionomer(s) are premixed and added to a drilling fluid.

27. The method of claim 1 further comprising the copolymer(s) and/or ionomer(s) are added to remedial fluid.

28. The method of claim 1 further comprising the copolymer and/or ionomer is added to wellbore treating fluid in an amount in the range of about 5 to 100 lbs/barrel.

29. The method of claim 28 wherein the copolymer and/or ionomer is added in an amount in the range of about 10 to 50 lbs/barrel of fluid.

30. The method of claim 1 further comprising the drilling fluid is selected from water-based and non-aqueous based.

31. A wellbore treatment composition comprising one or more copolymer(s) of ethylene acrylic acid and ethylene methacrylic acid, or the single valence ionomer(s) thereof, added to drilling fluid in an amount in the range of about 5 to 100 lbs/barrel.

32. The treatment composition of claim 31 wherein the single valence ionomers are single valence metal salt ionomers.

33. The treatment composition of claim 32 wherein the single valence metal salt ionomers are selected from single valence ionomers formed by reaction of the acidic groups on the copolymer(s) with alkaline salts of sodium, potassium, and lithium, or ammonia/ammonium (NH₄+/NH₃+).

34. The treatment composition of claim 31 further comprising the copolymer(s) and/or single valence ionomers thereof have acid numbers in the range of about 20 to 180.

35. The treatment composition of claim 31 further comprising the copolymer(s), or partially neutralize ionomer(s), are added as solid particles of different sizes.

36. The treatment composition of claim 35 wherein the particles are selected from the group consisting of pellets, prills, beads, granules, or powders.

37. The treatment composition of claim 31 further comprising the copolymers and/or ionomers are utilized as dispersions.

38. The treatment composition of claim 31 further comprising optionally adding at least one divalent or multivalent ion selected from the group consisting of alkaline earth metal ions and transition metal ions.

39. The treatment composition of claim 38 wherein the divalent or multivalent ion is selected from the group consisting of ZnO, MgO, CaCO₃, Zn(OH)₂, Zn(CO₃)₂ and lime, and combinations thereof.

40. The treatment composition of claim 31 in combination with any other solid bridging agents or fillers or additives known in the art utilized for lost circulation.

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