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(57) Abstract: A method of retarding the flow of water in a subterranean formation that includes injecting a gelling pill into the formation, the gelling pill comprising: brine; a crosslinkable polymer; and a crosslinkant; and allowing the crosslinkable polymer to crosslink to form a gel in the subterranean formation is disclosed. A water absorbing polymer is optionally included.

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DIVERTING AGENTS FOR WATER SHUT OFF

BACKGROUND OF INVENTION

Field of the Invention

[0001] Embodiments disclosed herein relate generally to methods and compositions for retarding or inhibiting the flow of water in a subterranean formation.

Background Art

[0002] Hydrocarbons accumulated within a subterranean hydrocarbon-bearing formation are recovered or produced therefrom through production wells drilled into the subterranean formation. When production of hydrocarbons slows, one or more injection wells may be drilled into the formation, into which fluid may be injected to enhance production by displacing or sweeping hydrocarbons through the formation so that they may be produced from production well(s). One type of such recovery operation uses field water or field brine as the injection fluid, which is referred to as a waterflood. Fluids injected later can be referred to as driving fluids. Although water is the most common, injection and drive fluids can include gaseous fluids such as steam, carbon dioxide, and the like.

[0003] While conventional waterflooding is generally the most cost effective method for obtaining additional hydrocarbons from a reservoir, it has a number of shortcomings. Foremost among these shortcomings is excess water and decreased oil production in some of the offset producing wells in the field and not in others, which results in increased production costs and reduced oil production rate. In many instances, poor performance is thought to be a result of water moving rapidly through high permeability channels or through natural or induced fractures. Induced fractures are often the result of over-pressuring the formation at some point. In other instances, water breakthrough may be related to permeability contrasts between different layers, which may or may not be in vertical communication in the reservoir.

[0004] Additionally, in some extreme cases, the waterflood channeling continues until a water breakthrough occurs such that large quantities of water drive fluid may channel directly from the injection well to a production well. This phenomenon most often occurs in heterogeneous reservoirs. When this occurs, not only are large volumes of water produced, which in and of itself is problematic, but also the fluid flow between the injection well and the production well likely bypasses pockets of oil.

[0005] Accordingly, there exists a continuing need for improvements in diverting agents and plugs to reduce or prevent water flow through a formation.

SUMMARY OF INVENTION

[0006] In one aspect, embodiments disclosed herein relate to a method of retarding the flow of water in a subterranean formation that includes injecting a gelling pill into the formation, the gelling pill comprising: brine; a crosslinkable polymer; and a crosslinkant; and allowing the crosslinkable polymer to crosslink to form a gel in the subterranean formation.

[0007] In another aspect, embodiments disclosed herein relate to a method of retarding the flow of water in a subterranean formation that includes introducing an effective amount of a gelling pill into flow channels in the formation, the gelling pill comprising: brine; a crosslinkable polymer; a crosslinkant; and a water absorbing polymer allowing the water absorbing polymer to permeate a region of the formation surrounding the flow channels; and allowing the crosslinkable polymer to crosslink to form a gel in the flow channel in the formation.

[0008] In yet another aspect, embodiment disclosed herein relate to a method of retarding the flow of water in a subterranean formation that includes injecting a gelling pill into flow channels in the formation, the gelling pill comprising: brine; a crosslinkable xanthan gum; and borate crosslinkant solids; and allowing the borate crosslinkant solids to permeate a region of the formation surrounding the flow channels; and triggering crosslinking between the xanthan gum and borate crosslink with magnesium oxide to form a gel in the subterranean formation.

[0009] Other aspects and advantages of the invention will be apparent from the following description and the appended claims.

DETAILED DESCRIPTION

[0010] In one aspect, embodiments disclosed herein relate to methods and diverting agents for retarding or inhibiting the flow of water through a region of a subterranean formation. As described above, during production operations, it is often desirable to retard or inhibit the flow of water through a particular region of a formation by adjusting its permeability. Such treatments/agents used are frequently referred to in the art as diverting treatments/agents as they divert a flow path of the fluid. The diverting agent of the present disclosure may be a hardened gel or plug of a crosslinked polymer formed in a formation, such as along a flow channel in the formation. To form such a diverting plug *in situ*, a gelling pill comprising a crosslinkable polymer and crosslinkant may be emplaced downhole. The gelling pills of the present disclosure also include a water absorbing polymer therein.

[0011] **Crosslinked Polymer**

[0012] The crosslinkable polymer of the present disclosure may be selected from any such polymers well known in the art. Representative polymers include various hydratable polysaccharides or polysaccharide derivatives such as xanthan gum, guar gum, hydroxyalkylguar, hydroxyalkylcellulose, carboxyalkylhydroxyalkylguar, wellan gum, gellan gum, diutan, scleroglucan, succinoglucan, various celluloses, biopolymers, and the like. The amount of crosslinkable polymer may vary; however, suitable amounts may range from 0.5 to 5 lb/bbl, depending on various factors such as the particular application, viscosity, etc.

[0013] In a particular embodiment, the crosslinkable polymer is preferably a xanthomonas gum (xanthan gum). Xanthomonas gum is a widely used viscosifier and suspending agent in a variety of fluids, which can be made by the fermentation of carbohydrate with bacteria of the genus Xanthomonas.

[0014] As a crosslinkant, any suitable crosslinking ion, metal containing species, or mixture of such ions and species may be employed. Accordingly, as used herein, the term “crosslinked” is understood to include crosslinking attributable to certain ions or metal containing species, such as borate ion. The crosslinking ions or species may be provided, as indicated, by dissolving into the solution compounds containing the appropriate ions/metals, or by other means. In a particular embodiment, the crosslinking ion is provided in a compound which only partial or sparingly partial solubility. Exemplary ions or metal containing species include those of boron, calcium, zinc, zirconium, and titanium, supplied from compounds such as boric acid, sodium borates, boron oxide, zirconium oxide, and titanium oxide. One of ordinary skill in the art would appreciate that depending on the conditions present when the crosslinkable polymer and crosslinkant are combined, crosslinking may be virtually immediate or may be delayed by means known in the art to allow for mixing and pumping of the gelling pill through surface equipment to be formed downhole *in situ*.

[0015] Such compounds may be provided as solid materials, and may have a broad size range. For example, in various embodiments, crosslinkant solids may range from 0.1 nm to 100 microns in size. One of ordinary skill in the art would appreciate that a particular size range may be selected depending on the particular application. For example, if it is desirable for the solids to permeate into the formation, smaller sized solids may be desirable. Further, the concentration of added crosslinkant may be dependent on factors such as the temperature, the amount of crosslinkable polymer employed, the firmness of the gel desired, and presence of water absorbing polymers (described below) and may range from up to 75 ppb (preferably up to 50, 30, or 25 ppb in various other embodiments) when water absorbing polymers are added to the pill and from up to 200 ppb (preferably up to 150, 100, or 50 ppb in various other embodiments). For example, when a pill is formed with the addition of the water absorbing polymers described below, to allow for the polymers to absorb any water (and swell), the formed gel should have sufficient flexibility for such phenomenon to occur. In such a situation, a lower amount of crosslinkant may be desirable. However, when no water absorbing polymers are included, greater amounts of crosslinkant materials may be desirable to form a firmer gel.

[0016] In a particular embodiment, hydrated borates of alkali metals and/or alkaline earth metals, such as sodium borates, calcium borates, and sodium calcium borates may be used as the crosslinkant. Ulexite, $NaCaB_5O_9 \cdot 8H_2O$, and probertite, $NaCaB_5O_9 \cdot 5H_2O$, are representative hydrated alkali metal alkaline earth metal borates. Colemenite, $Ca_2B_6O_{11} \cdot 5H_2O$, is a representative alkaline earth metal borate. Use of borates in such a mannaer is described in U.S. Patent No. 4,620,596, which is incorporated herein by reference.

[0017] When crosslinking xantham gum with a borate, a pH of at least 8, and a pH ranging from 8 to 13 and 9 to 12 in particular embodiments is necessary to initiate crosslinking. Thus, the addition of a crosslink initiator that will trigger the crosslinking may be used to allow for control of the gellation of the pill. Such control may allow for sufficient delay in the crosslinking so that the gelling pill may emplaced in a target zone and permeate the formation to any necessary extent prior to hardening/formation of the gel. In the embodiment where xanthan and borate are used to form the crosslinked polymer of the present disclosure, a crosslink initiator such as magnesium oxide, potassium hydroxide, etc that will raise the pH to trigger crosslinking may be used. DI-BALANCE™, which is commercially available from TBC-Brinadd (Houston, Texas) is an example of an inorganic oxide that may be used as a crosslink initiator in the embodiments disclosed herein. Further, one of ordinary skill in the art would also appreciate that other compounds such as lime, caustic soda, alkyl, aryl, and alkaryl amines, and calcium chloride. However, one of ordinary skill in the art would appreciate that some of these compounds may cause rapid setting and their use may be tailored depending on the application (e.g., when using small pills with fast pumping rates). Conversely, various alkyl, aryl, and alkaryl amines may be less soluble in the remainder of the pill and would therefore be slow to release their pH-increasing chemistry, resulting in a slow setting. Alternative slow-release crosslinking initiators would be obvious to one skilled in the art.

[0018] Depending on the conditions necessary for crosslinking to occur, one of ordinary skill in the art would appreciate that buffering agent(s) may also be used to affect the pH of the gelling pill to allow for greater control over crosslinking/gellation. Thus, the combination of a weak acid and its salts may be employed, including, for example, the corresponding acid and ammonium and alkali metal phosphates, carbonates, bicarbonates, sesquicarbonates, acetates, or mixtures thereof. Ammonium, potassium, and sodium carbonates, bicarbonates, sesquicarbonates and hydrogen phosphates are preferred as buffer salt components. However, one of ordinary skill in the art would appreciate that other compounds may be used, such as for example, diethanolamine. Proportioning of the buffer components of the combinations to achieve the desired pH is well within the ambit of those skilled in the art. The amount of buffer used may be an effective amount, *i.e.*, an amount sufficient to maintain the desired pH, given the additives and other components of the pill, which may range, for example, up to 50 pounds per 1000 gallons of fluid. Further, in a particular embodiment, acceleration or retardation of crosslinking may be achieved with the addition of calcium chloride or magnesium chloride, respectively. One of ordinary skill in the art would appreciate that use of an accelerant such as calcium chloride may find particular use in a cold temperature environment.

[0019] **Water Absorbing Polymer**

[0020] The water absorbing polymer may include crosslinked polyacrylamide, polyacrylate, or copolymers thereof. Particularly, the water absorbing polymer may include a copolymer of polyacrylamide that may be crosslinked internally via amide groups or an additional crosslinking agent, or two strands of sodium polyacrylate crosslinked with bis(acrylamide). The amount of water swellable polymer may vary; however, in a particular embodiment, a suitable amount may range from 0 to 30 lb/bbl.

[0021] In other embodiments, the water absorbing polymer may include carboxylate containing polymers such as polyacrylates, polyaspartates, and polylacetates, sulfonate containing polymers, quaternary or cationic amine containing polymers such as polyallylamine or polyethyleneimine, and polyacrylamide, polyvinyl alcohol gels, and polyurethane gels. Water absorbing polymers and the process for making such polymers suitable for embodiments of the present disclosure, include those described in U.S. Patent Nos. 4,618,631, 4,698,404, 4,755,560, 6,222,091, 6,376,072, and 6,750,262, which are herein incorporated by reference in their entirety. Some of these various water absorbing polymers have had specific application in the disposable diaper and agricultural water retention industries because of their ability to absorb up to 400 times their weight in water.

[0022] The absorbance capacity of the water absorbing polymers may be explained by the matrix-like structure of dry water absorbing polymer particle. The dry polymer may contain charged species within the matrix, such that the ionization of the polymer will cause the matrix network to open and create cavities that may absorb water by capillary action. Water absorbed into the polymer may be retained by hydrogen bonds that form between the charged species and the water. The actual mechanism for water absorbance and retention may vary based on the structure of a particular water absorbing polymer. For example, sodium polyacrylate, in the dry powdered state, contains a coiled backbone, lined with carboxyl groups. When exposed to an aqueous solution, the carboxyl groups dissociate into negatively charged carboxylate ions, which may repel one another along the polymer chain.

[0023] The repelling carboxylate ions thereby widen the polymer coils and allow water to move into contact with inner carboxyl groups, further continuing the widening or swelling of the polymer. Water is retained within the polymer due to hydrogen bonding between the water and the carboxylate ions on the polymer. Polyacrylamide, another water absorbing polymer, is structurally similar to polyacrylate but substitutes amide groups for the carboxyl groups on the polymer backbone. Free, unlinked amide groups, because they contain $-NH_2$ groups, can form hydrogen bonds with water. Further, because of the crosslinking that exists in these water absorbing polymers, the water absorbing polymers remain insoluble in an aqueous solution.

[0024] In specific embodiments, gelling pills employ POLYSWELL™, available from M-I LLC (Houston, Texas), which is an anionic acrylamide based copolymer formulation, as the water absorbing polymer component of the gelling pill.

[0025] **Base Fluid**

[0026] To prevent premature swelling of the water absorbing polymers of the present disclosure, an aqueous base fluid other than fresh water may be used. Such base fluids may include an aqueous fluid such as fresh water, sea water, a brine containing organic and/or inorganic dissolved salts, liquids containing water-miscible organic compounds and combinations thereof and similar compounds that should be known to one of skill in the art. However, one of ordinary skill in the art would appreciate that the selection of the base fluid may depend, for example, on the hydration of the crosslinkable polymer and/or the presence of a water absorbing polymer, so as to allow for hydration of the crosslinkable polymer yet minimize the amount of water absorbance by the water absorbing polymer prior to placement in the formation.

[0027] Brines suitable for use as the base fluid of the pills disclosed herein according to various embodiments of the present disclosure may include seawater, aqueous solutions wherein the salt concentration is less than that of sea water, or aqueous solutions wherein the salt concentration is greater than that of sea water. The salinity of seawater may range from about 1 percent to about 4.2 percent salt by weight based on total volume of seawater. The solutions, depending on the source of the seawater, typically contain metal salts, such as but not limited to, transition metal salts, alkali metal salts, alkaline earth metal salts, and mixtures thereof. Exemplary salts include halides of zinc, calcium, and mixtures thereof. For example, the solution can include zinc halide, such as zinc bromide or zinc chloride or both, optionally in combination with calcium bromide or calcium chloride or both. Salts that may be found in seawater include, but are not limited to, sodium, calcium, aluminum, magnesium, potassium, strontium, and lithium salts of chlorides, bromides, carbonates, iodides, chlorates, bromates, formates, sulfates, silicates, phosphates, nitrates, oxides, and fluorides. Salts that may be incorporated in a given brine include any one or more of those present in natural seawater or any other organic or inorganic dissolved salts. Additionally, brines that may be used in the drilling fluids disclosed herein may be natural or synthetic, with synthetic brines tending to be much simpler in constitution. In one embodiment, the density of the drilling fluid may be controlled by increasing the salt concentration in the brine (up to saturation). In a particular embodiment, a brine may include halide or carboxylate salts of mono- or divalent cations of metals, such as cesium, potassium, calcium, zinc, and/or sodium. The brine solution can include the salts in conventional amounts, generally ranging from about 1% to about 80%, and preferably from about 20% to about 60%, based on the total weight of the solution, although as the skilled artisan will appreciate, amounts outside of this range can be used as well. In a particular embodiment, the brine may be a NaCl or KCl brine.

[0028] Aging Temperature

[0029] In various embodiments, the gel mechanism may be temperature dependent. Thus, some gelling pills may preferentially cure at elevated temperatures such as about 60 to 100°C, while yet others may cure at higher temperatures such as 100-200°C. However, one of ordinary skill in the art would appreciate that, in various embodiments, the reaction temperature may determine the amount of time required for gel formation.

[0030] Time Required for Gel Formation

[0031] Embodiments of the gels disclosed herein may be formed by mixing a crosslinkable polymer, crosslinkant, and an optional crosslinking initiators. In some embodiments, a gel may form immediately upon mixing the components. In other embodiments, a gel may form within 1 minute of mixing; within 5 minutes of mixing in other embodiments; within 30 minutes of mixing in other embodiments. In some embodiments, a gel may form within 1 hour of mixing; within 8 hours in other embodiments; within 16 hours in other embodiments; within 80 hours in other embodiments; within 120 hours in yet other embodiments.

[0032] Gel Viscosity

[0033] In some embodiments, the pill may initially have a viscosity greater than water (for pumping purposes) yet low enough that the pill may effectively penetrate voids, small pores, and crevices, such as encountered in fine sands, coarse silts, and other formations. In other embodiments, the viscosity may be varied to obtain a desired degree of flow sufficient for decreasing the flow of water through or increasing the load-bearing capacity of a formation. The viscosity of the solution may be varied by increasing or decreasing the amount of base fluid relative to the polymer components, by employing other viscosifying agents, or by other techniques common in the art.

[0034] Gel Hardness

[0035] The reaction of the crosslinkable polymer and crosslinkant may produce gels having a consistency ranging from a viscous sludge to a hard gel. In some embodiments, the reaction of the two components may result in a soft gel. In other embodiments, the reaction may result in a firm gel and in a hard gel in yet other embodiments. The hardness of the gel is the force necessary to break the gel structure, which may be quantified by measuring the force required for a needle to penetrate the crosslinked structure. Hardness is a measure of the ability of the gel to resist to an established degree the penetration of a weighted test needle.

[0036] Hardness may be measured by using a Brookfield QTS-25 Texture Analysis Instrument. This instrument consists of a probe of changeable design that is connected to a load cell. The probe may be driven into a test sample at specific speeds or loads to measure the following parameters or properties of a sample:

springiness, adhesiveness, curing, breaking strength, fracturability, peel strength, hardness, cohesiveness, relaxation, recovery, tensile strength burst point, and spreadability. The hardness may be measured by driving a 4mm diameter, cylindrical, flat faced probe into the gel sample at a constant speed of 30 mm per minute. When the probe is in contact with the gel, a force is applied to the probe due to the resistance of the gel structure until it fails, which is recorded via the load cell and computer software. As the probe travels through the sample, the force on the probe and the depth of penetration are measured. The force on the probe may be recorded at various depths of penetration, such as 20, 25, and 30mm, providing an indication of the gel's overall hardness.

[0037] In some embodiments, the resulting gel may have a hardness value from 10 to 100000 gram-force. In other embodiments, the resulting gel may be a soft elastic gel having a hardness value in the range from 10 to 100 gram-force. In other embodiments, the resulting gel may be a firm gel having a hardness value from 100 to 500 gram-force. In other embodiments, the resulting gel may range from hard to tough, having a hardness value from 500 to 100000 gram-force; from 1500 to 75000 gram-force in other embodiments; from 2500 to 50000 gram-force in yet other embodiments; from 5000 to 30000 gram-force in yet other embodiments.

[0038] With respect to the variables listed above (i.e. temperature, time, etc.), those having ordinary skill in light of the disclosure will appreciate that, by using the present disclosure as a guide, properties may be tailored as desired.

[0039] Methods of Use

[0040] In accordance with various embodiments of the present disclosure, the various components of the gelling pill may be added simultaneously or in any combination separately to mix the polymer and crosslinkant within the formation to generate the gel in situ. Regardless of the order of emplacement, the gelling pill components will preferentially travel to the more permeable zones within the formation and gel, rendering these zones less permeable to subsequent fluid flow.

[0041] As stated above, the gelling pills and gels produced therefrom may find particular use as profile modification agents in enhanced oil recovery operations using injection of driving fluids such as water or other fluids to increase oil production. In particular, the pills may be useful for decreasing the permeability of selected portions of underground formations prior to or during secondary or tertiary recovery operations and also for water shut off treatments in producing wells or in communications between injection and producing wells.

[0042] For example, in an enhanced oil recovery operation, when a conventional waterflood or gas drive is performed and the drive fluid brakes through into the production well in excessive amounts, a gelling pill of the present disclosure may be pumped down the injection well and into the formation in any suitable manner and in any suitable amount, and for any desired length of time sufficient to obtain the desired in-depth penetration, gel formation and consequent permeability reduction in the high permeability zones (or flow channels) of the formation.

[0043] Such treatments may find particular use in rehabilitating a formation through which a conduit or flow channel connecting an injection well and producing well has been formed, such as naturally or induced fractures through the formation. By pumping a pill of the present disclosure into the conduit or flow channel, the crosslinkable polymer may crosslink to form a gelled plug. Without being bound to any particular mechanism, it is theorized that for pills consisting essentially of crosslinkable polymers and crosslinkants (without any water absorbing polymers), crosslinkant solids may be sufficiently small to invade or permeate the formation, which would result in a formed plug that has not only filled a conduit or flow channel, but has also stretched into the surrounding formation. Following gelling of the pill, the formation becomes part of the pill, providing added stability to the plug and formation, and reducing or preventing the likelihood of the plug being washed out.

[0044] It is also theorized for pills possessing water absorbing polymers therein that following the formation of the gelled plug, any additional water (either formation water or injected water) that comes into contact with the pill will be absorbed by the water absorbing polymer. It is further theorized that such absorbance will cause swelling of the polymer, pushing the pill further into the formation and formation lattice, and may provide additional stability to the particular area.

[0045] Alternatively, the formation may be treated prior to carrying out the fluid drive secondary recovery operations. This may be particularly applicable where there is good knowledge of the nature of the formation. Thus, in a formation where the oilbearing strata are interspersed with more permeable porous strata which contain no oil or an insufficient amount of oil to make secondary recovery operations economical, but which more permeable strata would still act as a thief zone, the formations may be treated in accordance with the embodiments of the present disclosure prior to initiating the fluid drive operation.

[0046] In still another embodiment, the pills may be applied to producing wells, either oil wells or gas wells, where there is a more porous nonhydrocarbon-bearing strata adjacent the hydrocarbon-bearing strata. For example, such a condition can exist where there is water sand adjacent the hydrocarbon-bearing sand and the water intrudes into the borehole and interferes with the production of hydrocarbons. In such instances, the formation may be treated in accordance with the present disclosure to shut off the flow of water. The method of carrying out such a water shutoff treatment is substantially the same as described above in connection with fluid drive operations. It is also within the scope of the invention to carry out the gel injection techniques of the present disclosure periodically or intermittently, as needed, during the course of a fluid drive secondary operation, or during the production of oil from a producing well.

[0047] In all of the above operations, the injection of the gelling pill of the present disclosure may be carried out in any conventional manner. Gels injected in accordance with the present disclosure may be prepared in advance, stored in suitable tanks, and then pumped into the well; or said gels may be formed in a conduit leading to the injection well, or in the tubing in the well itself, and then injected into the formation, or may be formed *in situ*. If desired, selected portions of the formation may be isolated mechanically, as by the use of packers, and other means known to the art, for treatment in accordance with the present disclosure. Further, spacer slugs as known in the art, such as a NaCl or KCl slug, may be used to lead and/or follow the gelling pill slug, or may be used to separate gel components when emplacing the components sequentially.

[0048] Further, as the crosslinking and gel formation of the present disclosure are pH dependent, should any placed pill need to be removed, etc., an acidizing treatment may allow for the removal of the plug formed downhole.

[0049] **Exemplary Formulations**

[0050] One formulation for one example of gelling pill that may be used is shown below in Table 1. FLOVIS® PLUS (a xantham gum) and POLYSWELL™ (an anionic acrylamide based copolymer) are available from M-I LLC (Houston, Texas). DI-BALANCE™ (magnesium oxide) is available from TBC-Brinadd (Houston, Texas). The pill is formulated by adding the FLOVIS® PLUS, ulexite (borate ore), and DI-BALANCE™ together in the NaCl brine, followed by the addition of the POLYSWELL™, and allowing the pill to set up.

Table 1

10.0 PPG NaCl	bbl	0.915
FLO-VIS® PLUS	grams	1.0
Ulexite (fine ground)	grams	25.0
DI-BALANCE	grams	12.0
POLYSWELL™ (ultra fine dry)	grams	21.0

[0051] Another formulation for a gelling pill that may be used is shown below in Table 2. FLOVIS® PLUS (a xantham gum) and POLYSWELL™ (an anionic acrylamide based copolymer) are all available from M-I LLC (Houston, Texas). DI-BALANCE™ (magnesium oxide) is available from TBC-Brinadd (Houston, Texas). The pill is formulated by adding the FLOVIS® PLUS, ulexite (borate ore), and DI-BALANCE™ together in the NaCl brine, followed by the addition of the POLYSWELL™, and allowing the pill to set up.

Table 2

10.0 PPG NaCl	bbl	0.915
FLO-VIS® PLUS	grams	2.0
Ulexite (fine ground)	grams	25.0
DI-BALANCE™	grams	12.0
POLYSWELL™ (ultra fine dry)	grams	14.0

[0052] Yet another formulation for a gelling pill that may be used is shown below in Table 3. FLOVIS® PLUS (a xantham gum) is available from M-I LLC (Houston, Texas). DI-BALANCE™ (magnesium oxide) is available from TBC-Brinadd (Houston, Texas).

Table 3

Fresh water	bbl	0.92
FLO-VIS® PLUS	ppb	3.0
Ulexite (fine ground)	ppb	50
Evaporated NaCl	ppb	18.0
DI-BALANCE™	ppb	12.0
Dry $CaCl_2$	ppb	25.0

[0053] Advantageously, embodiments of the present disclosure for at least one of the following. Modifying the fluid flow profile of the formation in the ways described above may provide a substantial decrease in the volume ratio of water:oil produced from the formation at production wells, thereby improving the overall oil recovery and economics of the operation. Moreover, the pill compositions of the present disclosure may provide a more permanent solution to troubling issues with water production. In particular, in addition to providing a diversion for immediate water flow, problems associated with subsequent water flows that have typically caused erosion of the formation and washing away of conventional diverting plugs may be minimized by the absorbance of such later appearing water by components within the originally placed pill.

[0054] While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.

CLAIMS

What is claimed:

1. A method of retarding the flow of water in a subterranean formation, comprising:
   injecting a gelling pill into the formation, the gelling pill comprising:
   brine;
   a crosslinkable polymer; and
   a crosslinkant; and
   allowing the crosslinkable polymer to crosslink to form a gel in the subterranean formation.

2. The method of claim 1, wherein the gelling pill, when gelled, retards water flow therethrough.

3. The method of claim 1, further comprising:
   producing oil from the subterranean formation.

4. The method of claim 1, further comprising:
   injecting a driving fluid into the subterranean formation.

5. The method of claim 1, wherein the gelling pill further comprises a crosslink initiator.

6. The method of claim 1, wherein the crosslinkable polymer comprises at least one of xanthan, guar, hydroxyalkylguar, carboxyalkylhydroxyalkylguar, scleroglucan, wellan, gellan, and diutan.

7. The method of claim 6, wherein the crosslinkable polymer comprises xanthan gum.

8. The method of claim 1, wherein the crosslinkant comprises at least one of boron, calcium, zinc, titanium, and zirconium.

9. The method of claim 8, wherein the crosslinkant comprises solid borates of alkali metals and/or alkaline earth metals.

10. The method of claim 9, further comprising:
    allowing the solid borates to permeate into the formation.

11. The method of claim 1, wherein the gelling pill further comprises a water absorbing polymer.

12. The method of claim 10, wherein the water absorbing polymer comprises crosslinked polyacrylamide, polyacrylate, or copolymers thereof.

13. A method of retarding the flow of water in a subterranean formation, comprising:
    introducing an effective amount of a gelling pill into flow channels in the formation,
        the gelling pill comprising:
        brine;
        a crosslinkable polymer;
        a crosslinkant; and
        a water absorbing polymer
    allowing the water absorbing polymer to permeate a region of the formation surrounding the flow channels; and
    allowing the crosslinkable polymer to crosslink to form a gel in the flow channel in the formation.

14. The method of claim 13, wherein the gelling pill, when gelled, retards water flow therethrough.

15. The method of claim 13, further comprising:
    producing oil from the subterranean formation.

16. The method of claim 13, further comprising:
    injecting a driving fluid into the subterranean formation.

17. The method of claim 13, wherein the water absorbing polymer absorbs water that flows into the region of the formation surrounding the flow channels having the gel formed therein.

18. The method of claim 13, wherein the gelling pill further comprises a crosslink initiator.

19. The method of claim 13, wherein the crosslinkable polymer comprises at least one of xanthan, guar, hydroxyalkylguar, carboxyalkylhydroxyalkylguar, scleroglucan, wellan, gellan, and diutan.

20. The method of claim 19, wherein the crosslinkable polymer comprises xanthan gum.

21. The method of claim 13, wherein the crosslinkant comprises at least one of boron, calcium, zinc, titanium, and zirconium.

22. The method of claim 21, wherein the crosslinkant comprises solid borates of alkali metals and/or alkaline earth metals.

23. The method of claim 13, wherein the water absorbing polymer comprises crosslinked polyacrylamide, polyacrylate, or copolymers thereof.

24. A method of retarding the flow of water in a subterranean formation, comprising:
injecting a gelling pill into flow channels in the formation, the gelling pill comprising:
brine;
a crosslinkable xanthan gum; and
borate crosslinkant solids; and
allowing the borate crosslinkant solids to permeate a region of the formation surrounding the flow channels; and
triggering crosslinking between the xanthan gum and borate crosslink with magnesium oxide to form a gel in the subterranean formation.