COMPOSITIONS CONTAINING WATER CONTROL TREATMENTS AND FORMATION DAMAGE CONTROL ADDITIVES, AND METHODS FOR THEIR USE

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ABSTRACT
The present invention relates to compositions of aqueous compositions comprising relative permeability modifier (RPM) macromolecules and one or more formation damage control additives, for use in treating hydrocarbon-producing wells, formations, and equipment, as well as methods for the use of such compositions. Such compositions, comprising the RPM macromolecule and the one or more formation damage control additive, such as a scale control agent, can result in the formation of a composition wherein the components exhibit a “synergistic” effect, whereby the ability of the formation damage control additive to prevent formation damage is enhanced relative to the use of the same additive separately.
FIG. 1
FIG. 2
FIG. 7
COMPOSITIONS CONTAINING WATER CONTROL TREATMENTS AND FORMATION DAMAGE CONTROL ADDITIVES, AND METHODS FOR THEIR USE

[0001] This application claims the benefit of U.S. Provisional Patent Application Ser. No. 60/601,466 filed Aug. 13, 2004, the contents of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The invention relates to treatments of subterranean formations to control water production and inhibit formation damage occurrence, and, more specifically, provides methods and compositions for controlling water production and formation damage occurrence simultaneously with a minimum number of steps.

BACKGROUND OF THE INVENTION

[0003] When a wellbore is initially drilled in a hydrocarbon-producing field, the hydrocarbon (i.e., oil or gas) extracted is typically dry, being substantially free of aqueous impurities. However, as the hydrocarbon reserves dwindle, or the formation becomes less producing, a progressively greater quantity of aqueous impurities begin to become mixed with the hydrocarbons. Certain locations are more prone to incorporating undesirable amounts of water with the produced hydrocarbon product, further raising the post-production costs involved in removing the water and purifying the hydrocarbon product and significantly reducing both the economic return and life of the well.

[0004] While there are numerous causes for this production including channeling through the cement casing, coming from bottom water drive reservoirs, high permeable and water-saturated streaks in the producing interval allowing water migration from water floods or edge water drive reservoirs, produced water is generally considered to be an inevitable consequence of water injection when water flooding is used to develop a hydrocarbon reservoir or when the field drive mechanism involves strong aquifer support.

[0005] During this same period of decreasing productivity, changes in physical conditions of the formation can generate both direct and indirect costs to the operator, and the water can simultaneously induce and sustain production changing/reducing formation damage within the hydrocarbon bearing formation.

[0006] For example, locations rich in minerals cause the formation of solid deposits in the production tubing and pipes, slowing the production of hydrocarbon product. Removal of these solid deposits (“scale”) slows production and increases the unit cost of the produced hydrocarbon product. Such occurrences of formation damage further compound the production problems. This is especially true in the instance of unwanted water production occurring at the same time, or just prior to, one or more additional formation damage occurrences.

[0007] Various chemical treatments have been developed for the treatment or prevention of water production and scale formation. A representative summary of these treatments follows.

[0008] U.S. Pat. No. 6,228,812 B1 (issued May 8, 2001) describes compositions that modify the permeability of subterranean formations, thereby reducing the production of water. The compositions contain copolymers such as a copolymer having a hydrophilic monomer, an anchoring monomer, and a filler monomer. The anchoring monomer is based on N-vinylformamide or N,N-diallylacetamide.

[0009] U.S. Pat. No. 4,708,974 (issued Nov. 24, 1987) offers injection of gel-forming phenolic compositions into a formation to reduce the amount of water produced with the desired hydrocarbon products. The gelled compositions have selective oil to water permeability, where the compositions are more permeable to oil than to water.

[0010] U.S. Pat. No. 6,720,291 (issued Apr. 13, 2004) describes a composition useful for prevention of downhole salt erosion in high-iron environments. The composition contains a first ingredient of sodium ferrocyanide and/or potassium ferrocyanide, and a second ingredient of phosphonic acid, and/or alkali and alkaline earth metal salts of a phosphonic acid.

[0011] U.S. Pat. No. 6,613,899 (issued Sep. 2, 2003) offers the use of carboxyl-containing fructans such as carboxymethylulinin for the prevention of scale deposits during oil production.

[0012] U.S. Pat. No. 6,527,983 (issued Mar. 4, 2003) presents a series of phosphonate compounds useful for the inhibition of scale formation in waters having a high barium content and low pH.

[0013] Clariant Oil Services (Aberdeen, UK) announced a new product named RELTREAT on Oct. 31, 2003. According to Clariant, “RELTREAT is a polymer based system which selectively shuts off or slows the production of unwanted water” during oil and gas production. North Sea users were reported to increase oil production from 413 to 1147 bbl/day. The water to oil ratio was reduced from over 20:1 to 8:1. Representatives of Clariant Oil Services presented information on the use of RELTREAT on the BP Miller field at the PEA Water and Gas Shut Off Forum on Nov. 6, 2003 in Sandnes, Norway.

[0014] While these various references describe either the reduction of water content or the inhibition of scale formation, none of them describe the simultaneous achievement of both desired results.

[0015] Other types of formation damage or damage to the various parts of the producing systems can also occur, such as hydrate formation, paraffin or wax deposition, and fine migration. For example, multiphase production and transport of hydrocarbon resources induces the coexistence of gas, water and eventually a liquid hydrocarbon phase (condensate or crude) at low temperature and under relatively high pressure. Such operation conditions can lead to hydrate crystals formation which can plug the equipment. Similarly, asphaltene coagulation and deposition can occur as a result of changes in parameters such as reservoir pressure, reservoir fluid temperature, and oil composition brought about by normal recovery operations. Likewise, oils with high wax content may cause pipeline plugging and deterioration of equipment, resulting in production shutdowns and economic losses.

[0016] While there are a number of approaches to these production problems in the patent and journal literature, nearly all of them deal with the problem on an individual
basis as they form, which can be costly when numerous problems arise during production. A further problem with such an approach is the cost off tracking and monitoring such production problems. For example, the technique of “downhole squeezing” is commonly used to address oil field scale formation, wherein control agent chemicals in a solution are injected into the near-wellbore area, using a preflush, squeeze, and overflush treatment before the well can be returned to normal function. However, the overflush process often flushes a significant portion of the control agent chemical from the rock surface, and the remaining control agent is gradually removed from the rock surface as oil production continues. Thus, further descaling treatments will be required.

[0017] There exists a need for compositions and methods which can minimize the steps of treating these conditions, while simultaneously achieving comparable or improved treatment results. The simultaneous inhibition of both of these challenges would greatly improve the efficiency and cost-effectiveness of a hydrocarbon producing well.

SUMMARY OF THE INVENTION

[0018] The present invention is directed generally to aqueous compositions comprising a relative permeability modifier (RPM) macromolecule and one or more formation damage control additives, for use in treating hydrocarbon-producing wells, formations, and equipment. Such compositions, comprising the RPM macromolecule and the one or more formation damage control additive, can result in the formation of a composition wherein the components exhibit a “synergistic” effect, whereby the ability of the formation damage control additive to prevent formation damage and to prevent the formation of particulates and deposits on pipes and tubing is enhanced relative to the use of the same additive separately.

[0019] The present invention is also directed to methods for controlling formation damage in hydrocarbon-producing formations, wells, and equipment, such as production tubing, wherein the method comprises introducing an aqueous treating solution comprising a RPM macromolecule and at least one formation damage control additive into the producing formation, well, or equipment, for a time and in an amount sufficient to control, reduce, or inhibit one or more types of formation damage. According to such methods, the aqueous treating solution can be pre-manufactured, or prepared directly on-site, immediately prior to the introducing step.

DESCRIPTION OF THE DRAWINGS

[0020] The following figures form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these figures in combination with the detailed description of specific embodiments presented herein.

[0021] FIG. 1 shows a graph of pressure (psi; y-axis) versus time (seconds; x-axis) for a 2% KCl brine control solution (mixture A).

[0022] FIG. 2 shows a graph of pressure (psi; y-axis) versus time (seconds; x-axis) for a sample containing scale control agent but no RPM (mixture B).

[0023] FIG. 3 shows a graph of pressure (psi; y-axis) versus time (seconds; x-axis) for a sample containing 90% scale control agent and 10% RPM (mixture C).

[0024] FIG. 4 shows a graph of pressure (psi; y-axis) versus time (seconds; x-axis) for a sample containing 75% scale control agent and 25% RPM (mixture D).

[0025] FIG. 5 shows a graph of pressure (psi; y-axis) versus time (seconds; x-axis) for a sample containing 50% scale control agent and 50% RPM (mixture E).

[0026] FIG. 6 shows a graph of pressure (psi; y-axis) versus time (seconds; x-axis) for a sample containing 10% scale control agent and 90% RPM (mixture F).

[0027] FIG. 7 shows a graph of pressure (psi; y-axis) versus time (seconds; x-axis) for a sample containing RPM but no scale control agent (mixture G).

DETAILED DESCRIPTION OF THE INVENTION

[0028] The present invention is directed generally to methods and compositions for controlling formation damage in a hydrocarbon-producing formation, as well as the tubing and equipment associated with producing a hydrocarbon from such formation. The method generally comprises introducing an aqueous treating composition into the formation, tubing, or equipment, wherein the aqueous treating composition comprising a relative permeability modifier (RPM) macromolecule and at least one formation damage control additive. Typically, the total amount of RPM macromolecule and formation damage control additive(s) in the aqueous treating composition is between from about 0.01 to about 70 volume percent. In a preferred mode, the weight ratio of RPM macromolecule to formation damage control additive in the composition is between from about 200:1 to about 1:200.

[0029] Suitable RPM macromolecules include, for example, anionic RPM macromolecules, anionic microgels which are crosslinked, and RPM macromolecules which are optionally deformable, all of which have a K-value from about 200 to about 1,000 and used at a concentration such that the viscosity of the treating fluid can range from about 1 to about 20 cP.

[0030] In one aspect of the present invention, a method for controlling formation damage in a hydrocarbon-producing formation that is susceptible to such formation damage is described, wherein the method comprises introducing an aqueous treating composition comprising an RPM macromolecule and at least one formation damage control additive into the hydrocarbon-producing formation. The RPM macromolecule and the formation damage control additive can have a synergistic relationship, in accordance with this aspect of the invention.

[0031] In a further aspect of the present invention, a method for treating formation damage in a hydrocarbon-producing well susceptible to such damage is described, wherein the method comprises injecting into the well an aqueous treating composition comprising a RPM macromolecule and at least one formation damage control additive. In accordance with this aspect of the invention, the RPM macromolecule and at least one of the formation damage control additives can have a synergistic relationship.
In yet another aspect of the present invention, a composition comprising a RPM and at least one formation damage control additive is described. The RPM macromolecule may be ionic or non-ionic. For instance, in accordance with this aspect of the invention, such RPM macromolecules include anionic RPMs, crosslinked RPM microgels, anionic RPM microgels, and anionic RPM microgels which are crosslinked. The formation damage control additives include scale control agents, salt control agents, fines control agents, organic deposit control agents, such as paraffin control agents and asphaltene control agents, hydrate control agents, corrosion control agents and/or mixtures thereof.

In accordance with a further aspect of the present invention, a composition comprising a RPM macromolecule and at least one scale control agent is described. In accordance with this particular aspect, the RPM macromolecule can be an anionic RPM macromolecule, such as an anionic crosslinked microgel, combined with the scale control agent(s).

Compositions can further comprise water or an aqueous solvent mixture. The water can generally be any aqueous solution such as distilled water, fresh water, salt water ("brine"), acid, etc. The composition can further comprise one or more additional solvents.

The compositions may be used in concentrate or working forms. The concentrate compositions can be prepared with or without water. The working compositions can be prepared by adding an appropriate amount of water or aqueous solution to a concentrate composition. Alternatively, the working composition can be prepared by sequentially or simultaneously adding at least one formation control additive and at least one RPM to water without first preparing a concentrate composition.

The concentrate compositions can generally contain the formation control additive and RPM at any concentration higher than the desired final working composition. The amount of concentrate added to water to prepare a desired concentration in the working composition can be easily calculated using the ratios of the two concentrations. For example, a 250 ppm concentrate would require a tenfold dilution to achieve a 25 ppm working composition. The concentrate compositions can generally have any concentration greater than the working composition. For example, the concentration can be about 5×, about 10×, about 15×, about 20×, about 25×, about 50×, about 100×, or ranges between any two of these values. Higher concentrations are possible, and would require higher dilution values.

Relative Permeability Modifiers

The compositions of the present invention are aqueous treatment compositions containing one or more RPM macromolecules. The RPM macromolecule may be any relative permeability modifier. For instance, a suitable RPM for use in the invention may be a polymer which can either impede the production of water and/or redirect water through permeable formation materials. Further, a RPM can be a macromolecule effective to selectively reduce the production of water from subterranean formations by modifying the permeability of the formation. Suitable as RPM macromolecule are deformable, polymeric compositions that comprise at least one hydrophilic monomer which aids in the RPM adhering to the formation and adds to the water/brine solubility; and at least one anchoring monomeric unit to cause the RPM to adhere to the formation. Further general characteristics of the RPM macromolecules as used herein include those RPM macromolecules having K-values (Fikentscher’s K-value, is a measure of a polymer’s average molecular weight) from about 200 to about 1,000 (which can be controlled by the concentration of the starting monomers and/or the amount of crosslinking), and those RPM macromolecules that are crosslinked, or both. Typically, the concentration of the RPM macromolecule in the aqueous treatment composition is from about 100 ppm to about 5,000 ppm.

Such RPM macromolecules also include soft microgels, which as used herein refers to those RPM macromolecules which may be crosslinked during their manufacture and have a weight average molecular weight of from about 10^6 to 10^9 g/mol. Typically, the microgel is crosslinked in an amount from about 0.25 to about 2.5 weight percent, based on the weight of the microgel. Further, such microgels can optionally and equally be described as having a size of from about 0.001 microns in diameter to about 100 microns in diameter.

In another aspect of the present invention, the RPM macromolecules can be used herein are anionic, crosslinked, water-soluble macromolecules which are readily pumpable and injectable, homogenous, and have a K-value, measured according to standard test methods (e.g., ISO 1628-2 (DIN 53726)), in the range from about 200 to about 1,000. Typically, the RPM macromolecules will have a K-value in the range from about 200 to about 500, and more typically a K-value in the range from about 250 to about 300.

Suitable RPMs include copolymers, homopolymers, or terpolymers comprised of hydrophilic monomers, at least one anchoring monomeric unit, an optional secondary anchoring unit, and one or more filler/spacer monomer units. Optionally, the RPMs can provide grafting sites for the inclusion of organosilicon compounds. Suitable RPM include those described in U.S. Pat. Nos. 5,735,349; 6,169, 058; 6,465,397; and 6,228,588, herein incorporated by reference. Optionally, and in accordance with the present invention, the RPM can include one or more organosilicon compounds. Preferred RPM macromolecules suitable for use within the present invention include Aquatech™, AQUATROL™, and AQUATROL™ V, all available from BJ Services Company (Houston, Tex.).

The RPM macromolecules suitable for use in the present invention have weight average molecular weights ranging from about 10,000 g/mol to about 50,000,000 g/mol, preferably from about 50,000 g/mol to about 5,000,000 g/mol, and more preferably from about 100,000 g/mol to about 2,000,000 g/mol. The RPM macromolecules for use herein are used at concentrations in the treating fluid such that the treating fluid has a viscosity from about 1 cP (0.001 Pa-s) to about 20 cP (0.020 Pa-s), and more preferably from about 1 cP (0.001 Pa-s) to about 5 cP (0.005 Pa-s), as measured by standard techniques.

The RPM macromolecule compositions of the present invention include copolymers, homopolymers or terpolymers comprising a hydrophilic monomeric unit; at least one first anchoring monomeric unit; and may also include at least one optionally selected second anchoring monomeric unit. A filler monomeric unit may also be...
employed. These copolymer compositions may be advanta-
geously used in aqueous-based water control treatment
fluids to selectively control water production from hydro-
carbon production wells.

As used herein, the term “monomeric anchoring unit” refers to components of a polymer that will preferen-
tially bind, by either physical or chemical processes, to subterranean formation material and which therefore tend to retain the polymer to the formation material. Anchoring
groups are typically selected to prevent a polymer from washing out of the formation due to fluid flow. Primary anchoring sites for the monomeric anchoring units are typically clay and feldspar surfaces existing in formation
pores, channels and pore throats. With benefit of this dis-
closure, those of skill in the art will understand that particu-
larly useful anchoring monomeric units are those having
aquaporin, quaternary nitrogen or functional groups capable of hydrolyzing to form amine-based anchoring
groups on the polymer. Examples include amide-containing
monomeric units.

Advantageously, the disclosed co-polymers having the first anchoring monomeric units described herein may be utilized in well treatment methods to selectively reduce the
permeability of a subterranean formation to water by a factor of about 10 or more, while at the same time leaving the
permeability of the formation to oil virtually unchanged.
Furthermore, the disclosed compositions, when introduced into a formation, tend to exhibit a high resistance to removal
from water bearing areas of the formation over time.

Hydrophilic monomers may include both ionic and
nonionic monomers. The term “nonionic monomer” refers
to monomers that do not ionize appreciably in aqueous
solution at near-neutral pH. Examples of suitable nonionic
hydrophilic monomers include, but are not limited to, vinyl
acrylamide comonomers including, but not limited to, acry-
lamide, N-vinyl acetamide, diacrylamidomethylacrylamide,
N-vinyl-N-methyl acrylamide, N,N-dimethyl acrylamide, N-vinyl-2-pyrrolidone, N-vinyl formamide (VF),
and N-ethyl-N-vinyl acetamide, as well as mixtures of two or more of such
comonomers. Ionic monomers may be either anionic or
cationic. Examples of anionic monomers include, but are not
limited to, alkaline salts of acrylic acid, ammonium or alkali
salts of acrylamidomethylpropane sulfonic acid (“AMPS”),
maleic acid, itaconic acid, styrene sulfonic acid, and vinyl
sulfonic acid (or its ammonium or alkali metal salts). Examples of suitable cationic monomers include, but are not
limited to, dimethyldiallyl ammonium chloride and quater-
nary ammonium salt derivatives from acrylamide or acryl-
cic acid such as acrylamidoethyltrimethyl ammonium chloride.

In one embodiment, one or more hydrophilic
monomeric units are typically employed and are based on
AMPS (such as at least one of ammonium or alkali metal salt
of AMPS, including sodium and/or potassium salts of
AMPS), acrylic acid, an acrylic salt (such as sodium acry-
late, N-vinyl pyrrolidone, ammonium or alkali metal salts
of styrene sulfonic acid, etc.), or a mixture thereof. It may be
desirable to employ ammonium or alkali metal salts of
AMPS for added stability, with or without one or more other
hydrophilic monomers, in those cases where aqueous treat-
ment and/or formation fluids contain high concentrations of
divalent ions, such as Ca$^{2+}$, Mg$^{2+}$, and the like.

Optional second anchoring monomeric units may
include any monomeric unit that will adsorb onto formation
material. In one embodiment, examples of optional second
anchoring monomeric units include at least one of dimeth-
yldiallyl ammonium chloride, ammonium or alkali metal
salts of acrylic acid, (such as sodium salts), vinyl phospha-
tate or vinyl phosphinate, or vinyl phosphate or a mixture
thereof.

Optional filler monomeric units may include any
monomeric unit suitable for copolymerization with the other
monomers in the composition. Desirable characteristics
of filler monomer units are the ability to retain water solubility
and/or relative low cost compared to other monomer units
present in a copolymer. Filler monomer units may be based
on, for example, monomers such as acrylamide, methylacry-
lamide, etc. In one embodiment, optional filler monomeric
units include monomers such as acrylamide, methylacryla-
mide, and the like.

With benefit of the present disclosure, the disclosed
compositions may be prepared using any method suitable for
preparing co-polymers known to those of skill in the art. In
one embodiment, monomers corresponding to the desired
monomeric units in the copolymer are selected and poly-
merized in an aqueous monomer solution.

In one exemplary embodiment, a first N-vinylfor-
manide monomer is combined with a hydrophilic monomer
(such as ammonium or alkali metal salt/s of AMPS) and a
filler monomer (such as acrylamides), in an aqueous base
fluid, typically water. Other 11 additives may include diso-
dium ethylenediamine tetraacetate (Na$_2$EDTA), pH adjust-
ing chemicals (such as potassium or sodium hydroxide,
carbonate, or bicarbonate), and a catalyst to initiate poly-
merization. Monomers with other anchoring groups may
also be present.

In addition to one or more salts selected from alkali
metal salts, alkali earth salts, formate salts, bicarbonate salts,
chloride salts, bromide salts, sulfate salts and acetate salts,
the composition for use in the invention may further include an
aqueous acid, such as hydrochloric, hydrobromic, acetic,
formic, citric, glycolic, gluconic, and hydrofluoric, and/or
mixtures thereof.

Any relative proportion of the disclosed monomers
that is suitable for polymerization and use in a water control
treatment fluid may be combined in an aqueous solution for
polymerization. However, in one embodiment, a first
anchoring monomer is combined to be present in an amount
of from about 2% to about 30% by weight of the total
polymer composition, alternatively from about 5% to about
15% by weight of the total polymer composition. In another
embodiment a first anchoring monomer is combined to be
present in an amount from about 2% to about 30%, alter-
atively from about 5% to about 15%, by weight of the total
polymer composition; ammonium or alkali metal salts of
AMPS is combined so that AMPS-based monomer is present
in an amount from about 0% to about 50%, alternatively
from about 20% to about 30%, by weight of the total
polymer composition; and acrylamide is combined to be
present in an amount from about 20% to about 98%, alternati-
vely from about 40% to about 65% by weight of the total
polymer composition. In one embodiment, N-vinylfor-
manamide is utilized as the first anchoring monomer.

Where necessary or desirable, the pH of a mon-
er solution may be adjusted or neutralized prior to poly-

merization by, for example, addition of a base such as sodium or potassium hydroxide, carbonate or bicarbonate. For example, the pH of an aqueous solution containing ammonium or alkali metal salts of AMPS may be adjusted to, for example, about 10 prior to the addition of N-vinylformamide and/or a second anchoring monomer or a filler monomer such as acrylamide. In one embodiment, a copolymer may be prepared by mixing the appropriate monomers into a tank of fresh water, followed by addition of a Na₂EDTA, pH adjuster and catalyst system to initiate polymerization. In one embodiment, ultimate pH range may be from about 4.5 to about 10.0 and alternatively from about 7.5 to about 9.5.

[0055] As indicated previously, and in accordance with the present invention, the RPM macromolecules of the present invention used as water redirecting agents may be crosslinked either internally, externally, or both. Such crosslinking is preferably performed using one or more chemical cross-linking techniques (vs. UV irradiation, biological crosslinking, etc.), and can occur during the synthesis of the RPM macromolecules, at the wellsite just prior to injection into an injector well (in the case of external crosslinking), or both. Crosslinkers suitable for use with the RPM macromolecules/microgels of the present invention include aldehydes, amides, acrylamides, isocyanates, metal salts, di- or poly-allyl based monomers, carbodiimide crosslinkers, and polyepoxide compounds. Most preferably, the RPM macromolecules of the present invention are crosslinked using aldehyde-based crosslinking techniques, acrylamide-based crosslinking techniques, or using polyepoxide compounds.

[0056] Examples of useful multifunctional crosslinking monomers include multifunctional acrylamides, and (meth)acrylates containing unsaturation at preferably 2, and optionally 3 or more sites on each copolymerizable comonomer molecule. In one embodiment, the multifunctional crosslinking monomers are selected from the group consisting of monomeric polyesters of acrylate or methacrylate acids and polyhydric alcohols; and monomeric polyalkenyl polyethers of polyhydric alcohols containing from 2 to about 6 polymerizable alkynyl ether groups per polyether molecule. Another exemplary crosslinking monomer is a monomeric polyester of an acrylic or methacrylic acid and a polyhydric alcohols containing from 2 to about 6 polymerizable α,β-unsaturated acrylic groups per polyether molecule. Other copolymerizable crosslinking monomers include divinyl ether, ethylene glycol dimethacrylate, (methylene-bisacylamide, allylpentaerythritol, and the like. The preferred crosslinking crosslinkers are somewhat water soluble and monomer soluble. Preferably, the acrylamide crosslinking agent used with the RPM macromolecules suitable for use in the methods of the present disclosure is methylene bis-acrylamide, or combinations of crosslinkers including methylene bis-acrylamide.

[0057] Aldehyde-based cross-linking techniques include those techniques using a reagent containing two reactive aldehyde groups to form covalent cross-links between neighboring amino groups of monomer residues in the RPM macromolecules described herein [Khor, E., Biomaterials, Vol. 18: pp. 95-105 (1997)]. Aldehydes suitable for use with the present invention include but are not limited to glutaraldehyde, formaldehyde, propionaldehyde, butyraldehyde and dialdehydes such as glyoxal. Preferably, the aldehydes are glutaraldehyde or formaldehyde.

[0058] Polypeoxy-based cross-linking techniques and agents include the use of compounds, such as short, branched polymers, terminating in reactive epoxy functionalities. Polypeoxy compounds suitable for use as cross-linking agents in the present invention include but are not limited to the epoxides of glycerol ethers, glycols, and glycerol polyglycidyl ethers.

[0059] Isocyanates are also suitable for use as cross-linking agents in the present invention. Generally, the isocyanates (R—NCO) react with primary amines to form a urea bond (R—H—CO—NH—R); difunctional isocyanates therefore have the ability to cross-link RPMs via lysine-like side chains. Isocyanates suitable for use as cross-linking agents in the present invention are preferably disocyanates, including biphienyl disocyanate, dimethoxy-4,4’-biphenyl disocyanate, dimethyl-4,4’-biphenyl disocyanate, 1,3-bis(isocyanatomethyl)benzene, phenyl disocyanate, tolune disocyanate, tolylene disocyanate, diisocyanato hexane, disocyanato octane, disocyanato butane, isophorone disocyanate, xylene disocyanate, hexamethylene disocyanate, octamethylene disocyanate, phenylene diisocyanate, and poly(hexamethylene disocyanate). Preferably, the isocyanate used as a cross-linking agent of the RPM macromolecules of the present invention is hexamethylene disocyanate.

[0060] Carbodiimide cross-linking agents and techniques can also be used within the scope of the present invention. These agents react with the carboxyl groups of monomers within the RPM macromolecules/microgels to form isocynure derivatives/iso-peptide bonds [Khor, E., ibid.]. Carbodiimides suitable for use as cross-linking agents with the RPM macromolecules of the present invention include but are not limited to N,N′-dicyclohexylcarbodiimide (DCC); N,N′-disopropylcarbodiimide (DIC); N,N′-di-tert-butylcarbodiimide; 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC; EDAC); water-soluble EDC (WSC): 1-tert-butyl-3-ethylcarbodiimide; 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide; bis(trimethylsilyl)carbodiimide; 1,3-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethyl)carbodiimide (BDCC, as described in U.S. Pat. No. 5,602,264); N-cyclohexyl-N′-(2-morpholinoethy) carbodiimide; N,N′-diethylcarbodiimide (DEC): 1-cyclohexyl-3-(2-morpholinoethyl)carbodiimide methyl-p-toluenesulfonate [e.g., Sheehan, J. C., et al., J. Org. Chem., Vol. 21: pp. 439-441 (1956)]; oligomeric alkyl cyclohexylcarbodiimides, such as those described by Zhang, et al. [J. Org. Chem., Vol. 69: pp. 8340-8344 (2004)]; polymer bound DCC; and polymer bound EDC, such as cross-linked N-ethyl-N′-(3-dimethylaminopropyl)carbodiimide on JANDAJEL™. Additionally, N-hydroxy succinimide (NHS), 1-hydroxy-7-azabenzotriazole (HATU), or similar reagents can be utilized in conjunction with the carbodiimide to minimize internal rearrangement of the activated isocynure derivative and provide more efficient cross-linking.

[0061] Other chemical cross-linking agents suitable for use in the present invention to provide cross-linked RPM macromolecules for use in redirecting formation water to improve hydrocarbon recovery from subterranean formations include but are not limited to homobifunctional crosslinkers such as BMME, BSOCOES, DSP (a thio-cleavable
cross-linker), DSS, EGS, water-soluble EGS, and SATA, as well as heterobifunctional cross-linking agents including GMB, MBS, PMPI, SMCC, SPDP, and MPH (maleimidopropionic acid hydrazide), MCH, EMCH (maleimidocapric acid hydrazide), KMUH (N-(k-Maleimidoundecanoic acid)hydrazide), and MPEH (44-N-MaleimidoPhenyl)butyric acid hydrazide), all available from Interchem (Cedex, France).

[0062] Specific examples of other crosslinking monomers suitable for use herein include but are not limited to trimethylol propane triacetate (TMPTA), trimethylol propane trimethacrylate (TPMPTA); diethylene glycol diacylate (DEGDA), diethylene glycol dimethacrylate (DEGDMA), trimethylol glycol diacylate, butylene glycol diacylate, methylene-bis-acrylamide, pentamethylene glycol diacylate, octylene glycol diacylate, glyceryl diacylate, glycelyl triacylate, neopentyl glycol diacylate, the tetracyclamine ester of pentaerythritol, as well as combinations thereof.

[0063] It is understood that certain unsaturated monomers may act in varying degrees to crosslink or branch the water soluble copolymer of the invention. For example, acrylate monomers with abstractable hydrogens, which can function as radical reactive sites, can in some embodiments of this invention, form a more branched or crosslinked polymer, thus affecting the preferred levels of the polyethylenic unsaturated crosslinking monomers. An example of a monounsaturated monomer with an abstractable hydrogen is 2-ethylhexyl acrylate.

[0064] Optional heat-reactive, latent carboxy- or hydroxy-reactive internal crosslinking systems can be provided by the incorporation of carboxylic-group containing comonomers, and N-alkylol amides, for example, N-methylol acrylamide, N-propyrolol acrylamide, N-methylol methacrylamide, N-methylol maleimide, N-methylol maleic acid esters, N-methylol-p-vinyl benzamide, and the like.

[0065] Known methods for optional post-polymerization crosslinking of carboxylic acid containing copolymers include, for example, U.S. Pat. No. 4,666,983 (crosslinking agent without any carrier solvent), using e.g. polyhydric alcohols, polyglycidyl ethers, polyfunctional amines and polyfunctional isocyanates. U.S. Pat. Nos. 4,507,438 and 4,541,871 utilize a difunctional compound in water with inert solvent or mixture of solvents. The difunctional compounds include glycidyl ethers, halosoptones, aldehydes and isocyanates with ethylene glycol diglycidyl ether crosslinker. The solvents include polyhydric alcohols with ethylene glycol, propylene glycol and glycercine enumerated as preferred polyhydric alcohols. U.S. Pat. No. 5,140,076 teaches a water-solvent-crosslinker mixture. Crosslinkers such as polyhydric alcohol, diglycidyl ether, polyaziridene, urea, amine and ionic crosslinkers are suggested.

II. Formation Damage Control Additives

[0066] In accordance with the compositions of the present invention, as well as the associated methods employing such compositions, at least one formation damage control additive is included in the composition. As used herein, the term “formation damage control additive” refers broadly to those compounds or compositions which can reduce the presence of damage, inhibit the formation of damage, or generally improve the well production profile following treatment of the well with such a compound or compositions. These formation damage control additives include, but are not limited to, scale control agents, salt control agents, fines control agents, paraffin or wax control agents, asphaltene control agents, hydrate control agents, corrosion control agents and mixtures thereof. Optionally, and in accordance with the present invention, one or more of these control additives can have an observable synergistic effect when combined with one or more RPM macromolecules.

A. Scale Control Agents

[0067] Scale formation, as used herein, can generally be thought of as a deposit of predominantly inorganic compounds. In this regard, a common process leading to scale formation in hydrocarbon production operations is the precipitation of sparingly soluble salts from oilfield brines. Some oilfield brines contain sufficient sulfate ion in the presence of barium, calcium, and/or strontium ions that the potential for forming barium sulfate (BaSO4) and/or strontium sulfate (SrSO4) scale exists. Often, the formation of scale results in reduced production and increased maintenance costs associated with the hydrocarbon production. Further, in some locations, naturally occurring radioactive materials have been found to incorporate themselves into the scale, resulting in health, safety, and liability concerns and increased scale disposal costs, in addition to the removal and/or inhibition of scale formation. Accordingly, scale control agents, as used herein, refer to those classes of compounds, specific compounds or mixtures, which act to reduce the occurrence, formation, or recurrence of scale, such as inorganic sulfate buildup and the like.

[0068] Scale control agents suitable for use herein can generally be any of the known scale control agents in the art. Typically, such scale control agents are ionic compounds and polymers. Examples of scale control agents suitable for use with the compositions of the present invention include, but are not limited to, polyelectrolytes, phosphonates, such as DETPMP, polyphosphonocarboxylic acids (PPCA), phosphonates, phosphates, and polymers such as polyacrylate (PAA), polyvinyl sulfonate (PVS), sulfonated polyacrylates, phosphomethylated polyanimes (PMPA), and the like. Typically, one class of ionic polymer suitable for use within the compositions of the present invention is the group of phosphonic carboxylic acid polymers. Suitable ionic polymers also include polyphosphonates, phosphonates, and polyphosphates. Specific examples of scale control agents suitable for use herein include diethylenetriamine penta(methyphosphonic acid), (DETPMP); hexamethylenediamine tetramethylenephosphonic acid (HMDP); phosphono poly-carboxylic acid (PPCA); nitrolotris(methylene) triphosphonic acid (NTP); Bellasol 30™ (an aqueous solution of a phosphonic carboxylic acid commercially available from OSP Microcheck, Inc.; Calgary, Alberta, Canada); the ACUMER™ polymer products, such as ACUMER™ 2100, a carboxylic/sulfonate copolymer commercially available from Rohm and Haas Company (Philadelphia, Pa.); and PSI-720 (BJ Services Company; Houston, Tex.), a phosphonic carboxylic acid polymer. Mixtures of phosphonates, phosphates, phosphates, polyphosphonates, polyphosphates, to polyphosphates, phosphonocarboxylic acid and its polymers, and polyalkylene phosphonic acid, such as BJ Services SCB-100 are also applicable. In addition, compounds such as glycolic acid, citric acid, gluconic acid, ethylenediaminetetraacetic acid, and other aminomethylcarboxylate compounds and derivatives used as metal chelating agents. All of
the above-mentioned scale control agents can be used in either their acid or salt forms. Salts are generally ammonium or alkali metal salts.

[0069] The concentration of scale control agent(s) in the compositions of the present invention can generally be any concentration suitable for inhibiting the formation of scale in a subterranean formation, in a wellbore, in pipe or tubing, or within hydrocarbon-producing equipment. Typical ranges of concentration of one or more scale control agents for use in the compositions described herein are from about 1 ppm to about 1000 ppm, more typically from about 5 ppm to about 100 ppm, for example from about 5 ppm to about 25 ppm. Specific examples of concentrations of scale control agents in the compositions of the present invention include about 1 ppm, about 5 ppm, about 10 ppm, about 15 ppm, about 20 ppm, about 25 ppm, about 30 ppm, about 35 ppm, about 40 ppm, about 45 ppm, about 50 ppm, as well as ranges between any two of these values. In one aspect, the concentration of scale control agent in the composition is about 25 ppm.

B. Salt Control Agents

[0070] Salt precipitation control agents, as used herein, refers to nitrilotriacetonitrile, nitrilotriacetamide or its derivatives, including salts of nitrilotriacetamides such as those described in U.S. Patent Application 2003/0173087. Generally concentrations of 25 to 1000 parts per million are used, or an amount necessary to inhibit salt (e.g., halite) crystallization.

C. Fines Control Agents

[0071] The formation fines, broadly defined as particles having a diameter of less than 44 microns, are ubiquitous in reservoir sandstones. These fines are mineralogically diverse and range in composition from clay minerals to non-clay siliceous minerals (i.e. quartz, feldspars, zeolites, silt, etc.). The significance of fines in hydrocarbon production and their potential permeability damage have been reported extensively. The two mechanisms by which clays cause permeability damage are swelling and migration. In swelling, fines such as clays (e.g. smectite, mixed-layer clays) imbibe water into their crystalline structures and subsequently increase in volume, plugging the pores in which they reside. In migration, clay and/or silt minerals (e.g. kaolinite, illite, chlorite) can be dispersed by contact with a foreign fluid or can be entrained by produced fluids and transported until a restriction, usually a pore throat, is encountered, where entrained particles bridge and restrict fluid flow. High fluid velocities, low salinities and high pH values are known to cause fines entrainment. Other non-clay fines known to cause permeability damage to sandstones are migrating quartz, feldspars, and zeolites particles.

[0072] Fines control agents, as used herein, refers to those agents which act to control, inhibit, suspend, or otherwise stabilize potentially mobile fines material. Such control agents include, but are not limited to, organosilane additives which react in situ to stabilize potentially mobile siliceous fines; organic polymer clay-control agents, and mixtures thereof; and mixtures of organophosphate or organophosphinophosphate compounds, and polyalkylenephosphonic acid, such as BJ Services SCB-100, or sodium acid pyrophosphate (SAPP).

D. Asphaltenes Control Agents

[0073] Asphaltenes are commonly defined as that portion of crude oil which is insoluble in heptane, are soluble in toluene, and typically exist in the form of colloidal dispersions stabilized by other components in the crude oil. Asphaltenes are often brown to black amorphous solids with complex structures, involving carbon, hydrogen, nitrogen, and sulfur. Asphaltenes are typically the most polar fraction of crude oil, and will often precipitate out upon pressure, temperature, and compositional changes in the oil resulting from blending or other mechanical or physicochemical processing. Asphaltene precipitation can occur in pipelines, separators, and other equipment, as well as downhole and in the subterranean hydrocarbon-bearing formation itself. Once deposited, these asphaltenes generally present numerous problems for crude oil producers, such as plugging downhole tubulars and/or wellbores, choking off pipes, and interfering with the functioning of separator equipment, all of which compound the production costs and require the need for remediation.

[0074] Asphaltene deposition/precipitation control agents suitable for use with the compositions and methods described herein include 2-hexadecyl naphthalene, sorbitan mono-oleate, decaglycerol tetraoleate, esters formed from the reaction of polyhydric alcohols with carboxylic acids, ethers formed from the reaction of glycidyl ethers or epoxides with polyhydric alcohols, esters formed from the reaction of glycidyl ethers or epoxides with carboxylic acids, combinations thereof, and the like. In addition, organic solvents based on terpenes such as d-limonene, a-pinene, and the like, are applicable.

[0075] Application of one or more asphaltene control agents according to the methods described herein may be made in combination with at least one RPM macromolecule and, optionally, one or more other formation damage inhibiting agents, by continuous or batch injection into the hydrocarbon-bearing formation itself, the well or wellhead system, or the hydrocarbon pipeline. It will be appreciated by those of skill in the art that there are a number of complex and interrelated factors which can determine the range of dosage of asphaltene control agent in a particular hydrocarbon stream, including but not limited to the chemical composition of the hydrocarbon or crude oil, and the temperature and pressure of the stream and the nature of any mechanical or physicochemical process the stream will be subjected to. The latter factor includes, but is not limited to, depressurization, cooling or heating, mixing with other produced fluids, shearing, the use of other additives, and the like. While it is nearly impossible to generalize about dosage levels due to these numerous and complex factors, it will be appreciated that in one non-limiting aspect, the proportion of asphaltene deposition control agent used in the compositions of the present invention can be at least about 10 ppm, typically in a range from about 15 ppm to about 500 ppm, and more typically in a range from about 100 ppm to about 300 ppm. Specific amounts of asphaltene control agents include about 20 ppm, about 25 ppm, about 50 ppm, about 75 ppm, about 100 ppm, about 150 ppm, about 200 ppm, about 250 ppm, about 300 ppm, about 350 ppm, about 400 ppm, about 450 ppm, about 500 ppm, as well as ranges and values between any two of these values, e.g., about 250 ppm, or a range from about 25 ppm to about 500 ppm.
E. Hydrate Control Agents

[0076] Natural gas hydrates comprise “cages” of water molecules enclosing “guest” molecules of natural gas, which occurs with sufficient combinations of temperature and pressure. Typical hydrate guest molecules include methane, ethane, propane, light hydrocarbons, methane-to-heptanes, nitrogen, hydrogen sulfide (H₂S), and carbon dioxide (CO₂). Natural gas hydrates can form during the production, gathering, and transportation of hydrocarbons in the presence of water at high pressures and low temperatures. Depending on the pressure and gas composition, gas hydrates can build up at any place where water coexists with natural gas at temperatures as high as 80° F. (about 30° C). Once formed, hydrates can deposit in the tubing, flow lines, and/or process equipment, thus restricting flow. In many cases, these restrictions eventually form plugs. Gas transmission lines and new gas wells are especially vulnerable to being at least partially blocked by hydrates. Hydrate plugs represent safety hazards as they contain significant volumes of compressed natural gas and have been known to destabilize, release large volumes of gas, and create safety concerns. As such, many in the industry feel it prudent to prevent hydrate plugs whenever possible, rather than trying to remediate them once they form.

[0077] Formation of gas hydrates can be eliminated or hindered by several methods. The thermodynamic prevention methods control or eliminate elements necessary for hydrate formation: the presence of hydrate forming guest molecules, the presence of water, high pressure and low temperature. The elimination of any one of these four factors from a system would preclude the formation of hydrates. Unfortunately, elimination of these hydrate elements is often impractical or even impossible. Transmission lines heating and insulating is a common mechanical solution to hydrate problems often encountered in long subsea pipelines. Hydrates will not form if the gas/water system is kept above the hydrate formation temperature. Gas dehydration is another method of removing a hydrate component. However, in a practical field operation, water can be economically removed to a certain vapor pressure only and residual water vapors are always present in a dry gas. Hydrate plugs in “dry” gas lines have been reported in the past.

[0078] Hydrate control agents, as used herein, refer generally to those chemicals added to the gas/water streams to prevent or inhibit hydrate formation. Typically the hydrate control agents in accordance with the present invention include methanol (MeOH) or ethylene glycol (MEG), both of which have been used to prevent natural gas hydrates in systems which operate inside the hydrate stability region. These chemicals function as thermodynamic hydrate control agents, shifting the conditions at which hydrates are stable and thus allowing the system to operate hydrate-free. Also suitable for use as hydrate control agents, in accordance with the present invention, are low-dosage hydrate control agents.

[0079] Low-dosage hydrate control agents (LDHAs) have been applied in numerous applications worldwide and continue to gain acceptance as alternatives to traditional methods of controlling hydrates. Whether used as retrofits to systems designed for use of MeOH or MEG, or used in systems specifically designed for LDHAs, LDHAs offer the distinct advantage of low dosage rates, often 1-10% that of MeOH or MEG. There are two commercially available types of LDHA chemicals available to control hydrates in hydrocarbon production, gathering, and transportation systems: anti-agglomerants (AAs) and kinetic hydrate control agents (KHCs). Both AAs and KHCs can be used as hydrate control agents in accordance with the present invention.

[0080] Anti-agglomerates (AAs) function by allowing hydrates to form but keeping the particles small and well-dispersed in the hydrocarbon liquid. Fluid viscosities remain low, allowing the hydrate particles to be transported along with the produced fluids without depositing. Because of this dispersion mechanism, true AAs function well, regardless of cooling and independent of how long the system remains in the hydrate region. These products do require the presence of sufficient liquid hydrocarbon to allow transportation of the hydrate particles, and as such are best suited to oil or gas condensate systems.

[0081] Kinetic control agents are a relatively new class of control agents developed to overcome gas hydrate problems, and are suitable for inclusion as formation damage control additives in accordance with the compositions and methods of the present invention. These additives have been designed to delay nuclei formation and to slow down their growth to form larger crystals. Kinetic control agents are generally water soluble polymers and are effective at low concentrations (<1% by weight with respect to water). A kinetic control agent suitable for use herein is HYTREAT™, a polymeric composition available from Clarient. Other useful compounds include polyether ammonium salts such as those described in U.S. Pat. No. 6,025,302.

F. Wax/Paraffin Control Agents

[0082] The phenomenon of wax deposits formation is common in petroleum industry and it occurs consequent to modifications in the thermodynamic variables that change the solubility of wax fractions present in petroleum. The paraffin deposition phenomenon involves saturated hydrocarbons of linear chain and high molecular weight during production, flow and treatment of petroleum. The deposition in subsea lines, surface equipment, production column, or even in reservoir rock can cause significant loss of petroleum production.

[0083] Precipitation and deposition of wax are associated with phase equilibrium of hydrocarbons and with fluid dynamic conditions of flow, respectively. The paraffinizing phenomenon is a function of the petroleum intrinsic characteristics and the temperature, velocity and pressure variations during production. The appearance of a solid phase in petroleum and the subsequent wax deposition are related to changes in the phase equilibrium, caused by petroleum cooling and/or separation of lighter fractions, originally dissolved in petroleum.

[0084] There are several preventive and/or corrective methods to control wax deposition: use of chemical control agents, injection of hot organic solvents and mechanical removal. In many cases, chemical treatments of paraffin or wax deposits have been stopgap or band-aid approaches that worked sporadically, if at all. The problem has been made particularly difficult because paraffin deposits vary significantly from reservoir to reservoir. Chemicals that are effective in one producing field are not always applicable in other reservoirs and even in various wells within the same reservoir (i.e., case specific). In association with the present
invention, it has been found that chemical treatments of paraffin or wax deposits using compositions of the present invention can elicit improved results.

[0085] Chemicals suitable for use as paraffin/wax deposition remediation agents include solvents, dispersants, and control agents, such as crystal modifiers and crystal disrupters, and are used to prevent paraffin crystals from forming massive crystal lattice structures which may plug tubing and process equipment. Suitable solvents include such hydrocarbons, as xylene, toluene and terpenes like d-limonene and a-pine. Terpenes can be dispersed or emulsified in aqueous solution in concentrations ranging from 2 to 70 vol. percent, or water, acid and brine solutions can be dispersed or emulsified in terpenes.

G. RPM Retention

[0086] The compositions described herein can also optionally include one or more additives for enhancing the anchoring capabilities of the RPM macromolecule to the formation substrate. Such additives include organosilane compounds, such as aminopropytriethoxysilane, or phosphonates, phosphinites, phosphates, polyphosphonates, polyphosphinites, polyphosphates phosphinocarboxylic acids and their polymers, or mixtures thereof.

[0087] Organosilane compounds suitable for use in the compositions of the present invention include, but are not limited to, organosilane alkoxides such as methyltriethoxysilane, dimethyldiethoxysilane, methyltrimethoxysilane, divinylmethoxysilane, divinyl-2-methoxyethoxy silane, di(3-glycidoxypropyl) dimethoxysilane, vinyltriethoxysilane, vinyl(tris-2-methoxyethoxy)silane, 3-glycidoxypropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, N-2-aminoethyl-3-propylmethyldimethoxysilane, N'-2-aminoethyl-3-propyltrimethoxysilane, N-2-aminoethyl-3-aminopropyltriethoxysilane, 3-aminopropytriethoxysilane, tetraethoxysilane and the like; and organosilane halides such as methylidichlorosilane, dimethylchlorosilane, methyltrichlorosilane, dimethyldibromosilane, diethylidichlorosilane, dipropyl/dibromosilane, butyl-trichlorosilane, phosphoryltribromosilane, diphenyldichlorosilane, tolyltribromosilane, methylphenyl dichlorosilane, propyldimethyloxysilane, and the like; amino silanes including 3-aminopropytriethoxysilane and N-2-aminoethyl-3-aminopropyltrimethoxysilane; Vinyl silanes including vinyl tris-(2-methoxyethoxy) silane, amionpropyl triethoxysilane, aminoethyl triethoxysilane, amionpropyl trimethoxysilane, aminoethyl trimethoxysilane, ethylene trimethoxysilane, ethylene triethoxysilane, ethyne triethoxysilane, and the like; and combinations of such organo silanes.

[0088] The weight ratio of RPM macromolecule to organosilicon compound in the aqueous composition, when such organosilicon compound is present, is generally from about 1:1 to about 200:1. The weight percentage of the RPM and organosilicon compound composite in the aqueous composition is generally from about 0.01 to about 50 weight percent. For instance, where the RPM macromolecule is PVA, the concentration ratio in parts per million of PVA RPM macromolecule to silicon in the organosilicon compound in the aqueous composition is generally from about 1:1 to about 200:1, preferably from about 30:1 to about 400:1. The weight percentage of the PVA RPM and silicon in the organosilicon compound composite in the aqueous composition is generally from about 1.0% to 24.0%, preferably from 3.0% to 10.25%, weight percentage. The concentration ratio in parts per million of polyacrylamide RPM macromolecule to silicon in the organosilicon compound in the aqueous composition is generally from about 10.1 to about 1:10, preferably from about 0.05:1 to about 1:0.5. The weight percentage of the polyacrylamide RPM and silicon in the organosilicon compound composite in the aqueous composition is generally from about 0.03% to 0.3%, preferably from 0.09% to 0.18%, weight percent.

[0089] The compositions as described herein, in addition to the RPM macromolecule and one or more formation damage control additives, can further comprise one or more additional components. For example, the compositions can further comprise one or more salts, including inorganic salts, such as alkali metal, alkali earth, and transition metal salts, and organic salts. Such salts include, but are not limited to, ammonium salts (i.e., tetramethylammonium chloride; ammonium chloride), calcium salts (i.e., CaCl2, CaBr2), magnesium salts, sodium salts, potassium salts (i.e., KCl, KBr), acetate salts (i.e., sodium acetate), formate salts, sulfate salts, carbonate salts, bicarbonate salts, and halide salts. Numerous examples of such suitable salts are known in the art. Further additives suitable for use in the compositions of the presently disclosed invention include additives for preventing, eliminating, or reducing emulsification of the treating fluids.

[0090] The pH of the compositions as described herein can generally be any pH compatible with the components of the composition, as well as with the piping, machinery, and equipment used during the drilling and production process and/or that the compositions will come into contact with. For example, the pH can be in the range from about 1 to about 9.5. Specific examples of suitable pH values include a pH of about 1, a pH of about 2, a pH of about 3, a pH of about 4, a pH of about 5, a pH of about 6, a pH of about 7, and ranges between any two of these pH values. A typical pH range in accordance with the presently described compositions is from about 4.5 to about 7. Such compositions are typically stable at room temperature (i.e., about 25° C.), and consequently do not form significant amounts of gel or precipitate following 3 or more days of storage at room temperature.

II. Methods of Use

[0091] The above-described compositions can be used to treat oil and gas producing wells, as well as subterranean, hydrocarbon-producing formations. The compositions described above, comprising at least one relative permeability modifier macromolecule and one or more formation damage control additive, are generally referred to herein as the “working compositions”. Such compositions can be prepared in advance and stored until use, or they can be prepared “on demand” at the work site. In accordance with this latter aspect, for example, the RPM macromolecule, formation damage control additive (i.e., scale control agent, asphaltene control agent, or both), and any additional components can be separate, and then are mixed to the desired concentration and pH at the wellsite as needed. This allows for the overall composition of the “working composition” to be adjusted as necessary, depending upon the specific problems or characteristics of the individual wellsites.

[0092] The working compositions can be introduced into a hydrocarbon producing well or hydrocarbon producing
subterranean formation using any means, such as by pumping through a wellbore, or injecting through an injector or producer well into a subterranean formation. The pumping or injecting can be through coiled tubing, conventional pipes, or other delivery systems. Typically, the working compositions are pumped at a sufficient volume and pressure such that they contact the downhole, subterranean formation for a time sufficient to act. For example, the compositions can be allowed to contact the formation for about 12 hours, by being “shut in.” Times of contact suitable for use with the compositions described herein will vary depending upon the individual composition, the needs of the well, and the desired result of the contact, but contact times can include ranges from about 2 hours to about 12 hours, from about 4 hours to about 10 hours, and from about 6 hours to about 8 hours. Specific examples of contact times suitable in association with the working compositions include about 2 hours, about 4 hours, about 6 hours, about 8 hours, about 10 hours, about 12 hours, and ranges between any two of these values. These treatments can also be pumped with carbon dioxide or nitrogen gases, either during the pumping of the treatment or after the treatment, as a flush. Pumping with the gases allows better coverage of the treatment interval, particularly as a means to increase contact with the formation, reduce the treatment volume and hence, the treatment cost.

Treatment of a hydrocarbon-producing well with the above-described compositions preferably results in at least the reduction of water production. Such treatments also preferably result in a reduction or inhibition of one or more types of formation damage, such as asphaltene deposition/precipitation, scale formation, salt precipitation, hydrate formation, and the like.

The reduction of water can be determined by any number of means, but typically it is determined by comparing water production before and after the treatment. The reduction of water is typically in the range from more than 0% to 100%.

The inhibition, prevention, or reduction in formation damage in association with the compositions of the present invention comprising both a RPM macromolecule and one or more formation damage control agents can be determined by comparing formation damage before and after treatment, or by comparing formation damage in two similar systems, one treated with the compositions of the present invention and one not treated with such a composition. For example, the installation of test nipples or other suitable monitoring devices within a flow line would enable visual inspection of the system to determine if scale formation or asphaltene deposition was reduced or inhibited. Similarly, periodic water analyses of water from the production system can indicate mineral content in the water, such as for example the calcium or barium content of the water in the production system. A decrease in the amount of specific, target minerals (e.g., barium or calcium) could indicate that the composition of the present invention was inhibiting scale formation. Formation damaging problems, such as scale formation, hydrate formation, salt precipitation, asphaltene deposition, and wax deposition can also be monitored, in accordance with the present disclosure, by monitoring parameters such as pressure, a method described specifically in the Examples below.

The compositions of the present invention can be used to treat, in addition to subterranean formation damage and wellbore damage, pipes and tubing associated with the production of oil and gas from wells. The presently described compositions can be passed through the pipe or tubing to prevent, reduce, or inhibit the formation of damage, e.g., scale formation, asphaltene precipitation, or salt precipitation, on or in the pipe or tubing. Typically, the passage of the “working composition” through the pipe or tubing can be achieved using pumping means known in the art. Other means of passing such compositions through the tubing or pipes include gravity flow means, vacuum, or combinations of such methods.

Use of the above-described compositions provides several advantages over the typical, step-wise application of well treatments, such as first injecting a water control composition into the formation, and after completion of such treatment injecting a scale control agent composition into the formation. A first advantage is that the simultaneous application of two or more materials (e.g., an RPM macromolecule and one or more formation damage control additives) is convenient, requires only one application, and is potentially more cost effective, allowing the well to return to production more rapidly. Another advantage, as described above and as specifically shown in the Examples below, the simultaneous application of an RPM macromolecule and at least one other material (e.g., a scale control agent) results in a synergistic effect, wherein the water control effect and/or the formation damage control effect (i.e., scale inhibition) is better than that achieved by applying either of the compositions separately. As a result, water control and improved formation damage control can be accomplished simultaneously, using one composition.

The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventors to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the scope of the invention.

EXAMPLES

Example 1

Preparation of Compositions Containing Scale Control Agent and RPM

PSI-720 (BJ Services Company; Houston, Tex.), a phosphinoacrylic acid polymer (prepared as a 50 wt. % solution in water) was selected as an exemplary scale control agent. AquaCon™ (BJ Services Company; Houston, Tex.), a polyacrylamide-based terpolymer containing sulfonated functional groups, was selected as an exemplary relative permeability modifier. A series of mixtures, A-G, were prepared at room temperature, as shown in Table 1, below.
TABLE 1

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Amt. PSI-720 (wt.%)</th>
<th>Amt. AquaCon™ (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (control)</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>C</td>
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</tr>
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<td>F</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>G</td>
<td>0</td>
<td>4000</td>
</tr>
</tbody>
</table>

2 wt. % KCl in water.

Example 2

Tube Blocking Test Results

[0100] A tube blocking test was used to assay the effect caused by combining a scale control agent and a relative permeability modifier, if any. The test system comprised peristaltic pumps, a mixing “tee”, a ¾-inch (0.3175 cm) coil of stainless steel tubing, and a 0.02 inch (0.05 cm) test coil of PEEK tubing.

[0101] Each of the mixtures described in Example 1 was mixed with test brine (2 wt. % potassium chloride in water) in an amount sufficient to give a final concentration of about 25 ppm PSI-720. This value was selected as it is slightly under the minimum scale to control agent concentration.

[0102] The two brine solutions were used to form a calcium carbonate scale precipitate. The first was a “cationic brine”, containing about 24,000 ppm sodium chloride, about 1,050 ppm sodium sulfate, about 6,610 ppm sodium bicarbonate, and about 4,610 ppm sodium acetate. The second brine was an “anionic brine”, containing about 24,000 ppm sodium chloride, about 1,340 ppm magnesium chloride, and about 1,470 ppm calcium chloride.

[0103] The mixture and the brines were pumped into the testing system and into the mixing “tee”, then into the stainless steel tubing, and finally into the test coil. Premature precipitation of the calcium carbonate scale was prevented by combining the cationic 20 brine and the anionic brine immediately before the test coil. The pressure on the system was measured using a pressure transducer. The transducer recorded the pressure at ten second intervals. A computer plotted the pressure against the elapsed time, as shown graphically in FIGS. 1-7. FIGS. 1-7 and their corresponding compositions are shown in Table 2.

TABLE 2

<table>
<thead>
<tr>
<th>Mixture</th>
<th>FIGURE</th>
<th>Amt. PSI-720 (ppm)</th>
<th>Amt. AquaCon™ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Control)</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>3</td>
<td>25</td>
<td>524</td>
</tr>
<tr>
<td>D</td>
<td>4</td>
<td>25</td>
<td>712</td>
</tr>
<tr>
<td>E</td>
<td>5</td>
<td>25</td>
<td>1,600</td>
</tr>
<tr>
<td>F</td>
<td>6</td>
<td>25</td>
<td>4000</td>
</tr>
<tr>
<td>G</td>
<td>7</td>
<td>0</td>
<td>4000</td>
</tr>
</tbody>
</table>

[0104] The blank control composition (containing brine but no scale control agent or relative permeability modifier, FIG. 1) exhibited a significant increase in pressure (in psi) after 600-800 seconds (about 10-14 minutes). The composition containing scale control agent (B; FIG. 2) effectively prevented any pressure increase in the test coil for a period of at least one hour (the tests were terminated after one hour, measured in seconds, s). A mixture was deemed to be “acceptable” if no significant increase in pressure (e.g., less than about 0.5 psi) was observed after one hour.

[0105] FIGS. 3, 4, 5 and 6 all show that the addition of a relative permeability modifier to the compositions did not adversely effect the ability of the scale control agent to prevent a significant increase in pressure (the concentration of scale control agent was held at about 25 ppm for these tests). A significant increase in pressure would suggest that the scale control agent was not working, or not working effectively. FIGS. 4, 5, and 6 (mixtures D, E, and F, respectively) exhibited remarkable inhibition of pressure increase. FIG. 7 (mixture G, containing only relative permeability modifier) showed an increase in pressure greater than the mixture containing scale control agent only (mixture B). However, both mixtures G and B exhibited a pressure increase less than that observed with the control (mixture A, containing only brine) shown in FIG. 1.

[0106] These results show that the addition of a relative permeability modifier to a brine solution containing a fixed concentration of scale control agent improves the inhibition of scale (as evidenced by the lack of pressure increase). These results suggest a “synergistic” effect of the two components.

Example 3

Stability of Compositions at Room Temperature

[0107] The mixtures prepared as described in Example 1 were kept at room temperature for three days. At the end of this period, no precipitation, gelling, or other signs of 10 incompatibility were observed.

[0108] All of the compositions, methods and/or processes disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions, methods and/or processes and in the steps or in the sequence of steps of the methods described herein without departing from the concept and scope of the invention. More specifically, it will be apparent that certain agents which are chemically related may be substituted for the agents described herein while the same or similar results would be achieved. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the scope and concept of the invention.

What is claimed is:

1. An aqueous treating composition comprising:
   a relative permeability modifier (RPM) macromolecule; and
   at least one formation damage control additive.
2. The aqueous treating composition of claim 1, wherein the RPM macromolecule is crosslinked.
3. The composition of claim 2, wherein the RPM macromolecule is crosslinked with microgel.
4. The composition of claim 3, wherein the microgel is crosslinked in an amount from about 0.25 wt. % to about 2.5 wt. %, based on the weight of the microgel.
5. The composition of claim 1, wherein the RPM macromolecule is ionic or non-ionic.
6. The composition of claim 1, wherein the RPM macromolecule has a K value from about 200 to about 1,000.
7. The composition of claim 1, wherein the RPM macromolecule has a weight average molecular weight from about 10,000 g/mol to about 50,000,000 g/mol.
8. The composition of claim 1, wherein the concentration of the RPM macromolecule in the composition is from about 100 ppm to about 5,000 ppm.
9. The composition of claim 1, wherein the at least one formation damage control additive is selected from the group comprising scale control agents, salt control agents, fines control agents, organic deposit control agents, hydrate control agents, corrosion control agents and mixtures thereof.
10. The composition of claim 1, wherein the at least one formation damage control additive is present in a concentration from about 1 ppm to about 1,000 ppm.
11. The composition of claim 1, further comprising one or more salts selected from the group consisting of alkali metal salts, alkali earth salts, formate salts, bicarbonate salts, chloride salts, bromide salts, sulfate salts and acetate salts.
12. The composition of claim 1, further comprising an aqueous acid selected from the group consisting of hydrochloric, hydrobromic, acetic, formic, citric, glycolic, gluconic, and hydrofluoric acid, and/or mixtures thereof.
13. The composition of claim 1, wherein the RPM macromolecule solution comprises an organosilicon compound.
14. The composition of claim 1, wherein the RPM macromolecule and the at least one formation damage control additive are synergistic.
15. The composition of claim 9, wherein the at least one formation damage control additive is a scale control agent.
16. The composition of claim 15, wherein the scale control agent is a phosphonate, phosphinate, phosphate, phosphonate, polyphosphinate, polyphosphate, or a phosphinocarboxylic acid or its polymers.
17. A method for controlling formation damage in a hydrocarbon-producing formation susceptible to formation damage, the method comprising introducing the composition of claim 1 into the hydrocarbon-producing formation.
18. The method of claim 17, wherein the RPM macromolecule is a crosslinked, deformable microgel.
19. The method of claim 17, wherein the concentration of the active components in the aqueous phase of the treating composition introduced into the hydrocarbon-producing formation is from about 0.01 to about 70 vol. %.
20. The method of claim 17, wherein the aqueous treating composition further comprises brine.
21. The method of claim 17, wherein the weight ratio of RPM macromolecule to formation damage control additive is between from about 200:1 to about 1:200.
22. The composition of claim 1, further comprising a hydrocarbon phase and an aqueous phase.
23. The composition of claim 22, wherein the at least one formation damage control additive is an organic deposit control agent.
24. The method of claim 17, wherein the composition further comprises a hydrocarbon phase and an aqueous phase.
25. The method of claim 24, wherein the at least one formation damage control additive is an organic deposit control agent.

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