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(54) **WATER FLOODING METHOD FOR SECONDARY HYDROCARBON RECOVERY**

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(57) **ABSTRACT**

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A water flooding composition in a method of secondary hydrocarbon recovery. The water flooding composition includes water and a thickening polymer. The thickening polymer includes a hydroxyethyl cellulose backbone polymer having a molecular weight of between about 1,000,000 and about 2,000,000 and a hydrophobic modifier. The hydrophobic modifier has a substitution level in the thickening polymer of between about 0.1 percent and about 2 percent by weight of the thickening polymer. The hydrophobic modifier is an alkyl hydrocarbon based material containing between about 10 and about 24 unsubstituted carbon atoms per group. The thickening polymer has a concentration in the water flooding composition of between about 0.01 percent and about 1 percent by weight of the water flooding composition. The water flooding composition is formulated within these ranges so that the water flooding composition has a suitable viscosity/mobility and so that the water flooding composition is injectable.

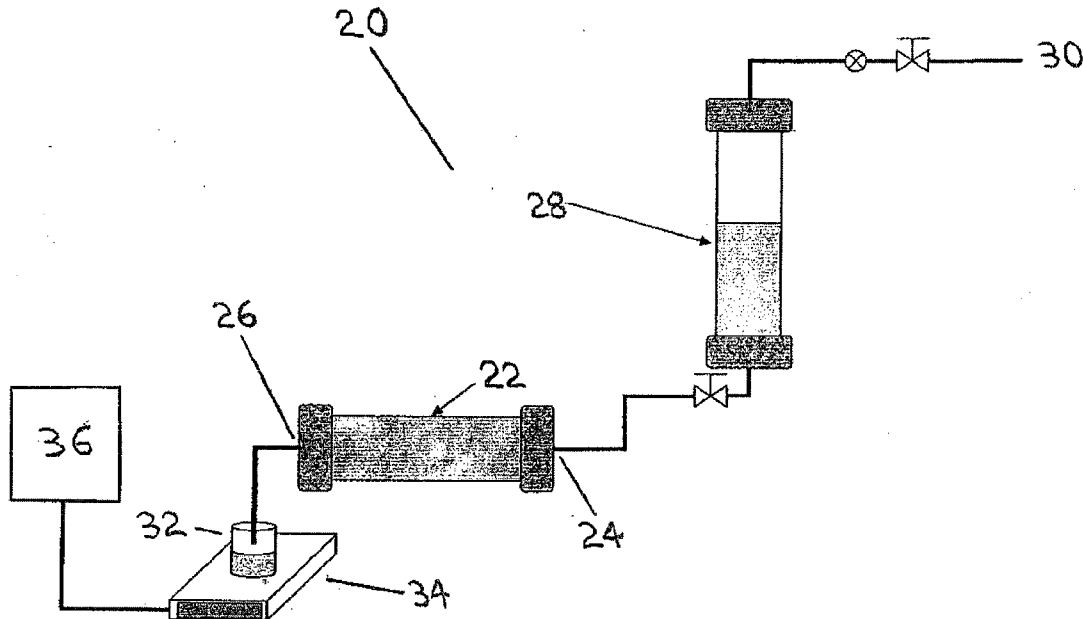
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THICKENING POLYMERS, WATER FLOODING COMPOSITIONS AND PROPERTIES									
Thickening Polymer	Molecular Weight	Hydrophobic Modifier Added (wt. % of Thickening Polymer)	Hydrophobe Substitution Level (wt. % of Thickening Polymer)	Thickening Polymer Concentration (wt. %)	Viscosity in Water (mPa.s) (at 7/s)	Viscosity in 1 % Brine (NaCl) (mPa.s) (at 7/s)	Viscosity in Hard Brine (at 7/s)	Injectability in Sandpack Test	Injectability in Coreflood Test/Oil Recovery
Flopaam 3630	18,000,000 to 20,000,000	N/A	N/A	0.15	249	25.8	14.5	Good	Good/Good
HMHEC 0421	720,000	6.25	0.57	0.2	4.8	5.2		Good	
HMHEC 0418	720,000	12.5	0.87	0.2	6.2	7.0		Good	
HMHEC 0611	720,000	18.75	1.1	0.2	10.7	11.9		Good	
HMHEC 1206	720,000	25	1.4	0.2	16.4	13.6 (sandpack filtration test) 31.9 (coreflood test)		Average	Poor/Poor
HMHEC 0721	720,000	25	1.6	0.2	45.5	48.9		Poor	
HMHEC 0422	1,300,000	6.25	0.58	0.2	10	10.1		Good	

Figure 1

THICKENING POLYMERS, WATER FLOODING COMPOSITIONS AND PROPERTIES									
Thickening Polymer	Molecular Weight	Hydrophobic Modifier Added (wt. % of Thickening Polymer)	Hydrophobe Substitution Level (wt. % of Thickening Polymer)	Thickening Polymer Concentration (wt. %)	Viscosity in Water (mPa.s) (at 7/s)	Viscosity in 1 % NaCl (mPa.s) (at 7/s)	Viscosity in Hard Brine (at 7/s)	Injectability in Sandpack Test	Injectability in Coreflood Test/Oil Recovery
HMHEC 0603	1,300,000	12.5	0.85	0.2	27.4	19.8 (sandpack filtration test) 33.4 (coreflood test)		Good	Good/Good
HMHEC 0603	1,300,000	12.5	0.85	0.17			39.8	Good	
HMHEC 0730	1,300,000	15	1.0	0.15		21.8		Average	Poor/Poor
HMHEC 0318	1,000,000	18.75	1.2	0.2		26		Good	
HMHEC 0318	1,000,000	18.75	1.2	0.162			28.7	Good	

Figure 1 (cont.)

FILTRATION TEST RESULTS										
Thickening Polymer	Filtration with Whatman # 1 Filter at 15 psi				Sandpack Filtration					
	Aqueous Medium	Concentration of Thickening Polymer (% by weight)	Filter Ratio	Concentration of Thickening Polymer (% by weight)	Pre-Injection Viscosity (mPa.s) (at 7/s)	Viscosity Following Injection of 1 Pore Volume (mPa.s) (at 7/s)	Viscosity Following Injection of 2 Pore Volumes (mPa.s) (at 7/s)	Permeability Ratio (k_{brine} after polymer-flooding composition)		
Flopaam 3630	1% NaCl	0.4	1.01	0.15	25.8	24.7	26.3	0.11		
HMHEC 0421	1% NaCl	0.19	1.58							
HMHEC 0418	1% NaCl	0.2	1.13	0.2	7.0	6.3	6.9	0.56		
HMHEC 0611	1% NaCl	0.2	1.52	0.2	11.4	9.5	11.4	0.47		
HMHEC 1206	1% NaCl	0.2	1.37	0.2	13.0	5.6	12.7	0.42		
HMHEC 0721	Water	0.2	1.24	0.2	48.9	2.5	3.8			
HMHEC 0422	1% NaCl	0.2	1.20	0.2	11.9	10.3	12.2	0.54		

Figure 2

FILTRATION TEST RESULTS									
Thickening Polymer	Filtration with Whatman # 1 Filter at 15 psi			Sandpack Filtration					
	Aqueous Medium	Concentration of Thickening Polymer (%) by weight	Filter Ratio	Concentration of Thickening Polymer (%) by weight	Pre-Injection Viscosity (mPa.s) (at 7/s)	Viscosity Following Injection of 1 Pore Volume (mPa.s) (at 7/s)	Viscosity Following Injection of 2 Pore Volumes (mPa.s) (at 7/s)	Permeability Ratio (k_{brine} after polymer-flooding composition)	
HMHEC 0603	1% NaCl	0.2	1.24	0.2	19.8	14.9	20.3	0.56	
HMHEC 0603	Water	0.25	1.09						
HMHEC 0603	Hard Brine	0.22	1.24	0.17	39.8	18.7	37.8	0.52	
HMHEC 0730	1% NaCl	0.15	1.07	0.15	21.8	11.4	20.5	0.38	
HMHEC 0318	Water	0.25	1.04	0.2	26.0	15.9	43.7	0.7	
HMHEC 0318	Hard Brine	0.16	1.07	0.162	28.7	8.2	33.9	0.7	

Figure 2 (cont.)

PROPERTIES OF TEST CORES			
Core Properties	HPAM Core	HMHEC 1206 Core	HMHEC 0603 Core
Core Type	Silica Sandpack AGSCO 3/0 (sieved to 200 mesh-75 mm), acid washed		
Weight (g)	477.82	475.1	467.87
Length (cm)	30.47	29.10	30.0
Diameter (cm)	3.81	3.81	3.81
Area (cm ²)	11.4	11.4	11.4
Bulk Volume (cm ³)	347.3	331.77	342.0
Porosity (Φ)	42.5	45.1	43.1
Pore Volume (ml)	147.5	149.77	147.5
Core Temperature (°C)	20	20	20
Net Overburden Pressure (kPa)	7000	7000	7000
Air Permeability (mD)	2504	3116	3710
Brine Permeability (mD)	2370	2723	2606
Oil Flow Rate (cm ³ /h)	4	4.2	3.6
Waterflood Rate (cm ³ /h)	4	4.2	3.6

Figure 3

OIL VISCOSITY AND DENSITY		
Temperature (°C)	Viscosity (mPa.s)	Density (g/m ³)
20	3587	0.9766

Figure 4

COREFLOOD TEST RESULTS			
Parameter	HPAM Core	HMHEC 1206 Core	HMHEC 0603 Core
K _o absolute (mD)	2868	2471	2980
Irreducible Water Saturation, fraction (S _{wir})	0.099	0.102	0.066
Initial Oil Saturation, fraction (S _{oi})	0.901	0.898	0.934
Water Saturation, fraction (S _w) (after initial water flood)	0.317	0.335	0.302
Water Saturation, fraction (S _w) (after 1 st 2.1 pore volumes (PV) of water flooding composition)	0.649	0.600	0.663
Oil Saturation, fraction (S _o) (after 1 st 2.1 pore volumes (PV) of water flooding composition)	0.351	0.400	0.337
Oil Recovery (% OOIP) using Water (after 1.0 PV)	24.2	25.96	25.3
Water Flooding Composition	0.19 percent by weight Flopaam 3630	0.2 percent by weight HMHEC 1206	0.2 percent by weight HMHEC 0603
Oil Recovery (% OOIP) using Water Flooding Composition (after 2.1 PV)	36.8	14.4	38.6
Pre-Injection Viscosity (mPa.s) (at 7/s)	41.5	31.9	33.4
Post-Injection (Effluent) Viscosity (mPa.s) (at 7/s)	40.0 @ 2 PV	2 @ 2.7 PV 2.1 @ 3.9 PV 2.5 @ 4.3 PV	30.9 @ 2.3 PV

Figure 5

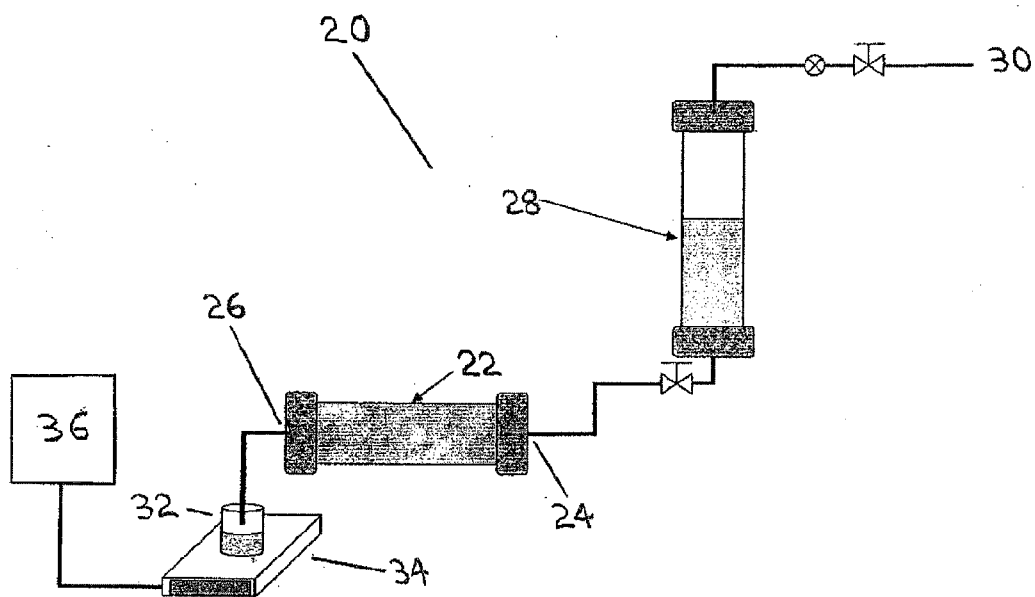


Figure 6

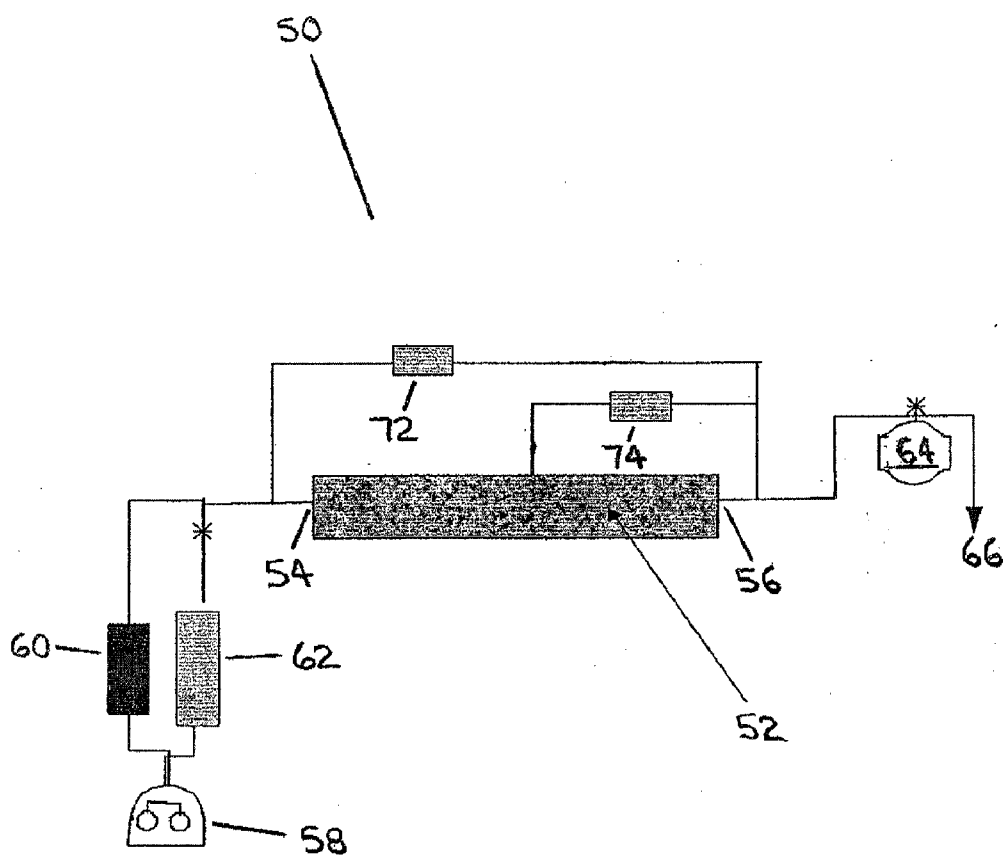


Figure 7

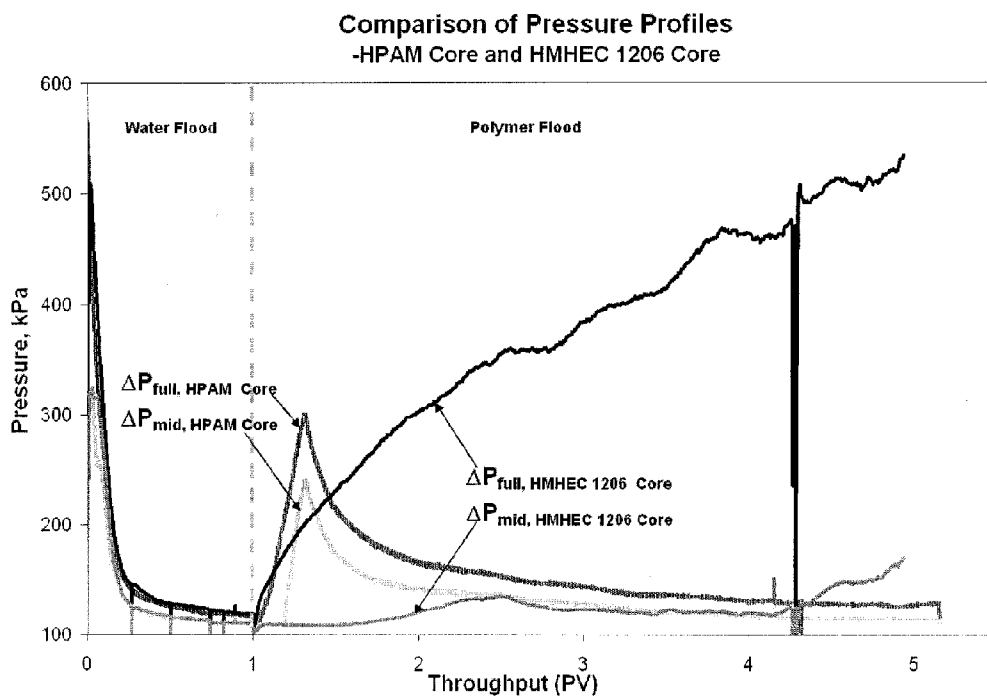
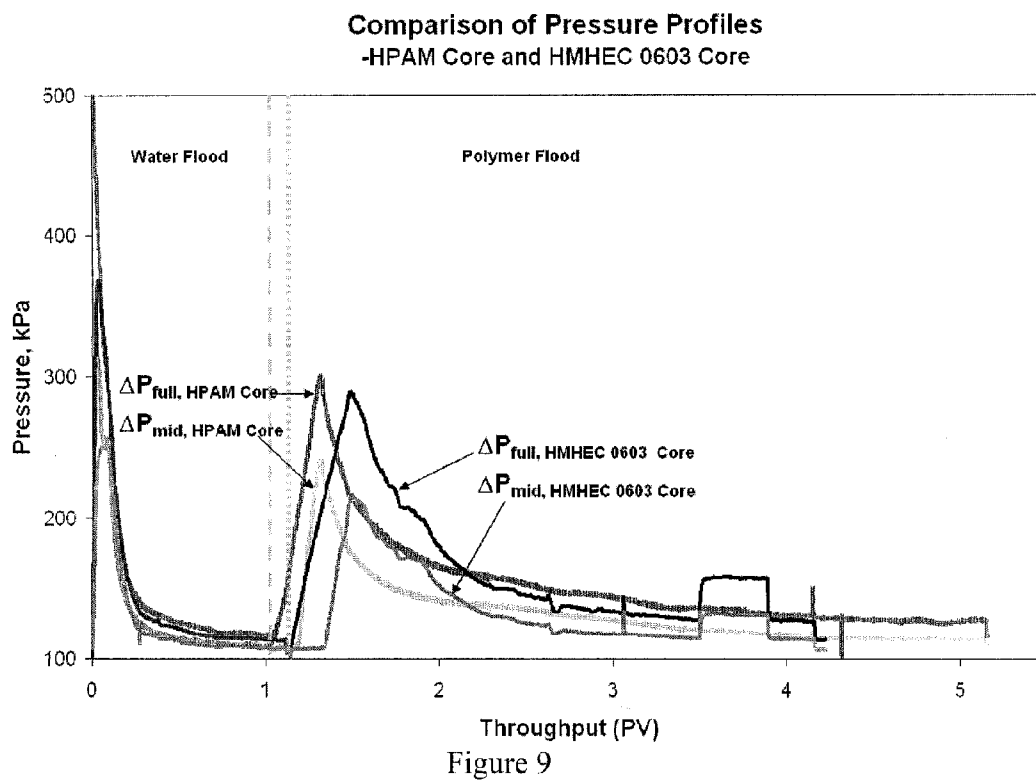


Figure 8



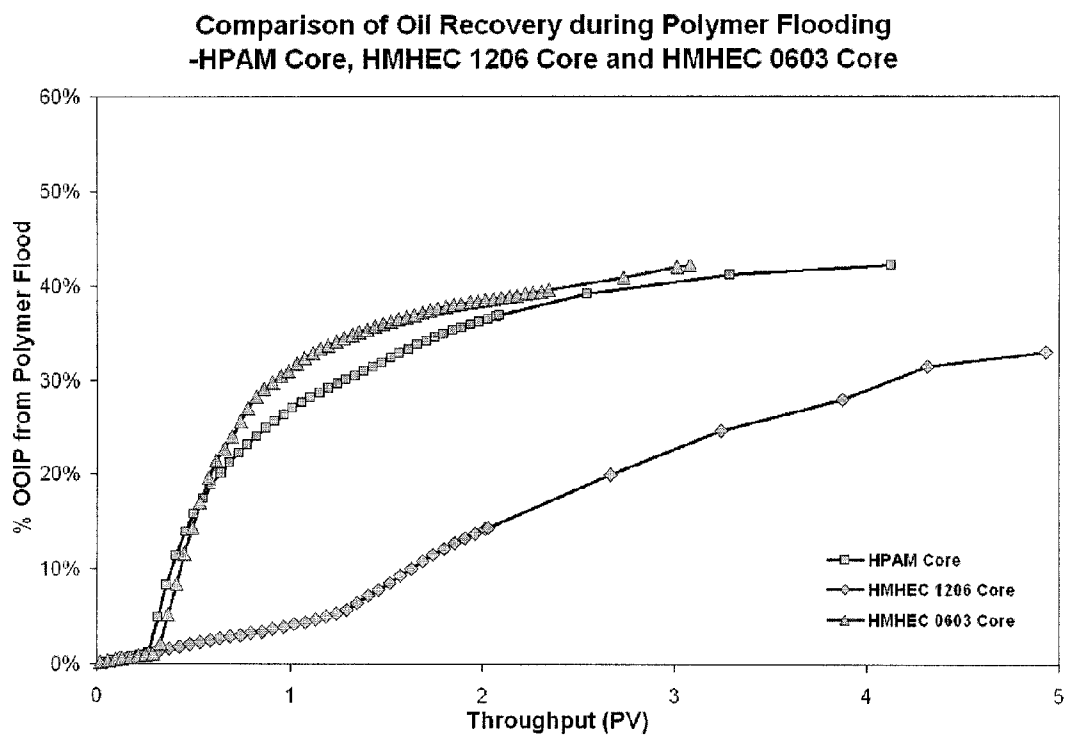


Figure 10

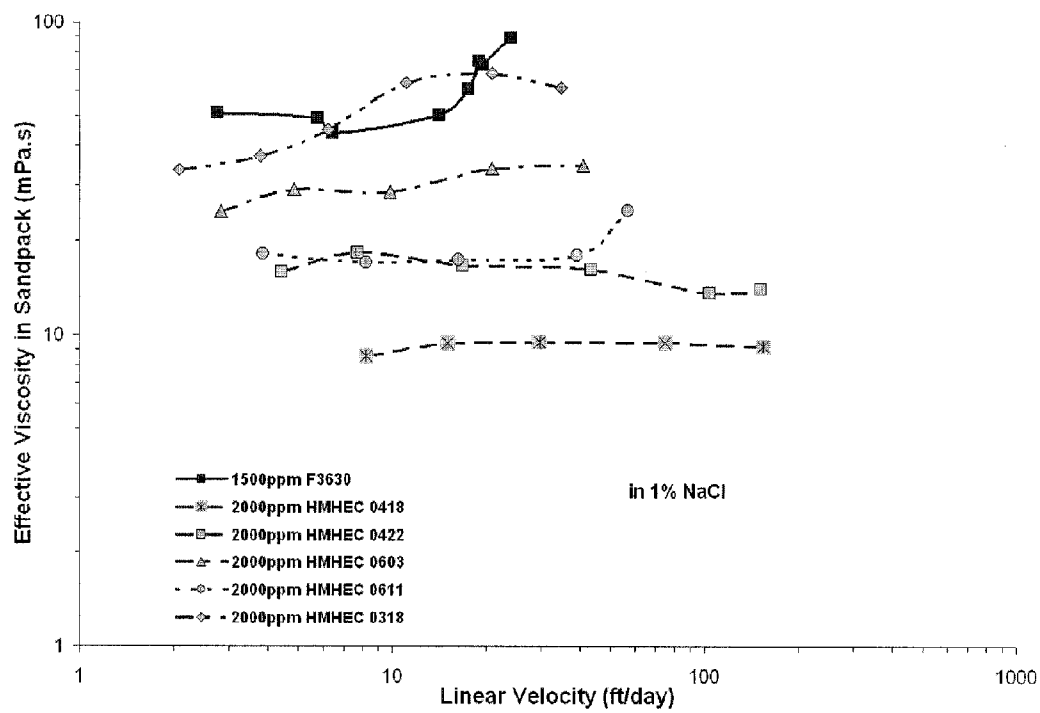


Figure 11

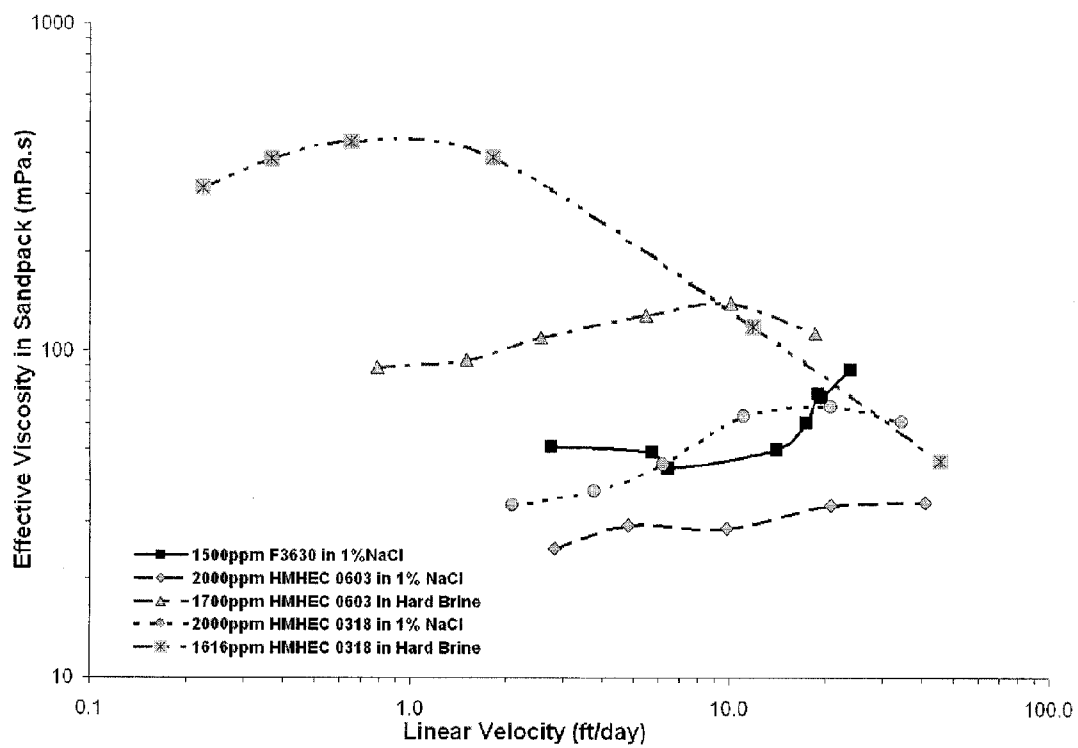


Figure 12

WATER FLOODING METHOD FOR SECONDARY HYDROCARBON RECOVERY

TECHNICAL FIELD

[0001] A method of secondary hydrocarbon recovery of the type which comprises passing a water flooding composition through a subterranean formation containing a hydrocarbon deposit.

BACKGROUND OF THE INVENTION

[0002] The first stage of hydrocarbon production is known as primary hydrocarbon recovery. In primary hydrocarbon recovery, energy (eg., pressure or potential energy) within the subterranean formation is utilized to displace hydrocarbons from the subterranean formation, into a production wellbore, and ultimately to the earth's surface. Primary hydrocarbon recovery may be assisted by artificial lift systems such as pumps or gas lift installations.

[0003] The second stage of hydrocarbon production is known as secondary hydrocarbon recovery. In secondary hydrocarbon recovery, an external fluid in gas or liquid form is injected into the subterranean formation through one or more injection wells. The external fluid typically functions to displace hydrocarbons through the subterranean formation toward one or more production wellbores through which the hydrocarbons may be produced to the earth's surface. The external fluid may also assist in maintaining or increasing the pressure in the subterranean formation.

[0004] One form of secondary hydrocarbon recovery is water flooding. In water flooding, a water flooding composition is injected into the subterranean formation as the external fluid. The water flooding composition is typically comprised of water and one or more other materials which function to provide desirable properties to the water flooding composition. Such other materials may include a thickener to increase the viscosity of the water flooding composition and thereby decrease the mobility of the water flooding composition through the subterranean formation. Suitable thickeners for use in water flooding compositions are often polymers, with the result that water flooding using a water flooding composition containing a thickener is sometimes referred to as polymer flooding.

[0005] Mobility of a fluid is defined as the ratio of permeability (of the medium through which the fluid is passed) to viscosity (of the fluid). Mobility is therefore a function of both the properties of the fluid and the properties of the environment in which the fluid is located.

[0006] A hydrocarbon deposit in a subterranean formation may exhibit a relatively high viscosity and a relatively low mobility. If a water flooding composition has a relatively lower viscosity and a relatively higher mobility than the hydrocarbon deposit, the water flooding composition may tend to move through the hydrocarbon deposit or to bypass the hydrocarbon deposit so that the hydrocarbon deposit is not effectively displaced toward the production wellbore or wellbores by the water flooding composition.

[0007] This phenomenon is described as "fingering", and results in a reduction in the "sweep efficiency" of the water flooding procedure. Sweep efficiency is defined as the ratio of the volume of the subterranean formation which is actually contacted by the water flooding composition during a water flooding procedure to the volume of the subterranean forma-

tion which is available to be contacted by the water flooding composition during the water flooding procedure.

[0008] Fingering can be reduced and sweep efficiency can be increased by including a thickener in the water flooding composition in order to increase its viscosity and thus reduce its mobility through the subterranean formation.

[0009] U.S. Pat. No. 4,529,523 (Landoll) describes a water flooding method for enhanced recovery of oil from a subterranean oil-containing formation using a water flooding medium which includes a thickener and which may also include a compatible surfactant.

[0010] In Landoll, it is suggested that the problems which may limit the effectiveness of water flooding procedures include high mobility of the water flooding medium, immiscibility of the water flooding medium with oil, and lack of durability of the water flooding medium when exposed to salts/brine, shear forces, heat, and/or biological activity. These problems are stated in Landoll to be overcome by the use of a water flooding medium which contains a hydrophobically modified, water-soluble polymer as the thickener.

[0011] In Landoll, the thickening polymer includes a polymer backbone which may be any nonionic, water soluble polymer including poly(acrylamide), a cellulose ether, poly(ethylene oxide), a natural polysaccharide gum, and poly(vinyl alcohol). The nonionic character of the backbone is stated to be important in promoting salt tolerance. Operable polymers in Landoll have molecular weights of about 50,000 to 1,000,000. Preferable molecular weights in Landoll are from about 150,000 to about 800,000.

[0012] The polymer backbone in Landoll is modified by the incorporation of small amounts of long chain alkyl groups. It is stated in Landoll that in general, the alkyl modifier contains from about 8 to about 25 carbons, preferably from about 16 to about 25 carbons. The alkyl modifier is stated to be present in an amount from about 0.2 percent by weight to the amount which makes the polymer less than 1 percent soluble in water, or from about 0.2 to about 2.0 percent by weight of the polymer.

[0013] The concentration of the polymer in the water flooding medium is stated in Landoll to be from about 0.01 to 2.0 percent by weight, preferably from about 0.1 to 0.5 percent by weight.

[0014] In Landoll, the preferred polymer is hydrophobically modified hydroxyethyl cellulose where the alkyl chain modifier is from about 8 to about 25 carbon atoms in length.

[0015] The nonionic, hydrophobically modified, water-soluble polymers in Landoll are described in Landoll as being especially well suited for use in polymer-water flooding media because they possess surface activity which may reduce or eliminate the use of a separate surfactant in water flooding procedures.

[0016] However, in addition to providing a water flooding composition which exhibits a suitable viscosity and mobility, another goal in formulating a water flooding composition is to provide a water flooding composition which is injectable through the subterranean formation. A water flooding composition is injectable if it can pass through the subterranean formation without causing significant plugging of the subterranean formation.

[0017] A water flooding composition which exhibits a suitable viscosity and mobility may be unsuitable for use as a water flooding composition if it does not exhibit sufficient

injectability. Injectability of the water flooding compositions is not a consideration which appears to be addressed in Landoll.

SUMMARY OF THE INVENTION

[0018] References in this document to dimensions, to orientations, to operating parameters, to ranges, to lower limits of ranges, and to upper limits of ranges are not intended to provide strict boundaries for the scope of the invention, but should be construed to mean “approximately” or “about” or “substantially”, within the scope of the teachings of this document, unless expressly stated otherwise.

[0019] The present invention is directed at methods of secondary hydrocarbon recovery of a type which comprises passing a water flooding composition through a subterranean formation containing a hydrocarbon deposit. The present invention is more specifically directed at improvements in the composition of the water flooding composition.

[0020] The water flooding compositions of the invention are comprised of water and a thickening polymer, wherein the thickening polymer is comprised of a hydroxyethyl cellulose backbone polymer having a molecular weight of between about 1,000,000 and about 2,000,000 and a hydrophobic modifier comprised of an alkyl hydrocarbon based material.

[0021] The hydroxyethyl cellulose backbone polymer may be described as “HEC”. The thickening polymer may be described as hydrophobically modified HEC or as “HMHEC”.

[0022] The hydroxyethyl cellulose backbone polymer has a hydroxyethyl molar substitution or “MS”, which is the average number of moles of hydroxyethyl which are incorporated in the polymer per anhydroglucose unit of the cellulose. In some embodiments, the MS of the hydroxyethyl cellulose backbone polymer is at least about 0.5. In some embodiments, the MS of the hydroxyethyl cellulose backbone polymer is at least about 1. In some embodiments, the MS of the hydroxyethyl cellulose backbone polymer is at least about 2. In some embodiments, the MS of the hydroxyethyl cellulose backbone polymer is between about 2 and about 2.5. In some embodiments, the MS of the hydroxyethyl cellulose backbone polymer is about 2.5.

[0023] In some embodiments, the hydroxyethyl cellulose backbone polymer may be comprised of a combination of different hydroxyethyl cellulose (HEC) polymers.

[0024] The alkyl hydrocarbon based material of the hydrophobic modifier may be comprised of any alkyl group and/or substituted alkyl group or any combination of alkyl groups and/or substituted alkyl groups. In some embodiments, the alkyl hydrocarbon based material of the hydrophobic modifier may be comprised of one or more alkyl groups and/or substituted alkyl groups which contain between about 10 and about 24 unsubstituted carbon atoms per group. In some embodiments, the alkyl hydrocarbon based material of the hydrophobic modifier may be comprised of one or more alkyl groups and/or substituted alkyl groups which contain between about 12 and about 18 unsubstituted carbon atoms per group.

[0025] As used herein, “unsubstituted carbon atom” means a carbon atom which is directly bonded only with hydrogen and/or carbon.

[0026] The water flooding compositions of the invention may be further comprised of other substances in addition to water and the thickening polymer. As non-limiting examples, the water in the water flooding composition may be present in

brine form (i.e., containing up to about 10 percent sodium chloride and/or other equivalent monovalent metal salts), as hard brine (i.e., brine containing up to about 0.4 percent divalent and/or polyvalent metal ions such as calcium or magnesium), and/or may contain other substances and/or impurities. The water flooding composition may also be further comprised of other materials for enhancing the properties of the water flooding composition or the effectiveness of the water flooding procedure.

[0027] The water flooding compositions of the invention are formulated to have a viscosity and/or mobility which is compatible with the viscosity and/or mobility of the hydrocarbon deposit which is intended to be produced using the water flooding method.

[0028] As used herein, “viscosity” means dynamic viscosity and is expressed in pascal-second (Pa·s) units at a shear of between about 7/s and about 10/s. As used herein, permeability is expressed in darcy (D) units. As used herein, mobility is the ratio of permeability to viscosity, where permeability is expressed in darcy (D) units and viscosity is expressed in pascal-second (Pa·s) units at a shear of between about 7/s and about 10/s.

[0029] In some embodiments, the viscosity of a water flooding composition may be considered to be compatible with the viscosity of a hydrocarbon deposit if the viscosity of the water flooding composition is between about 2 mPa·s and about 100 mPa·s. In some embodiments, the viscosity of a water flooding composition may be considered to be compatible with the viscosity of a hydrocarbon deposit if the viscosity of the water flooding composition is between about 5 mPa·s and about 50 mPa·s. In some embodiments, the viscosity of a water flooding composition may be considered to be compatible with the viscosity of a hydrocarbon deposit if the viscosity of the water flooding composition is between about 5 mPa·s and about 40 mPa·s.

[0030] In some embodiments, the mobility of a water flooding composition may be considered to be compatible with the mobility of a hydrocarbon deposit if a ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than about 100:1. In some embodiments, the mobility of a water flooding composition may be considered to be compatible with the mobility of a hydrocarbon deposit if a ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than about 50:1. In some embodiments, the mobility of a water flooding composition may be considered to be compatible with the mobility of a hydrocarbon deposit if a ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than about 10:1. In some embodiments, the mobility of a water flooding composition may be considered to be compatible with the mobility of a hydrocarbon deposit if the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than about 2:1.

[0031] The water flooding compositions of the invention are also formulated to be injectable into the subterranean formation in which the water flooding method is to be performed. Generally, a water flooding composition may be considered to be injectable into the subterranean formation if it can pass through the subterranean formation without causing significant plugging of the subterranean formation. Plugging of the subterranean formation may result when one or more constituents of the water flooding composition become

separated from the water flooding composition during the water flooding procedure and remain in the subterranean formation after the water flooding composition has passed through the subterranean formation.

[0032] Plugging of the subterranean formation may be indicated by a decrease in the viscosity of the water flooding composition as it passes through the subterranean formation and/or by a decrease in the concentration of the thickening polymer in the water flooding composition as the water flooding composition passes through the subterranean formation. Plugging of the subterranean formation may also be indicated by a decrease in the permeability of the subterranean formation as the water flooding composition passes through the subterranean formation.

[0033] In some embodiments, the injectability of a water flooding composition may be evaluated by passing the water flooding composition through a permeable test medium. In some embodiments, the injectability of a water flooding composition may be evaluated by considering the properties of the water flooding composition before and after the water flooding composition has been passed through the permeable test medium. In some embodiments, the injectability of a water flooding composition may be evaluated by considering the properties of the water flooding composition at an upstream end of the permeable test medium and a downstream end of the permeable test medium. In some embodiments, the injectability of a water flooding composition may be evaluated by considering the permeability of the permeable test medium before, during and/or after the water flooding composition has been passed through the permeable test medium.

[0034] The water flooding composition may have an initial viscosity at an upstream end of the permeable test medium and a final viscosity at a downstream end of the permeable test medium. In some embodiments, the injectability of the water flooding composition may be evaluated having regard to the initial viscosity of the water flooding composition and the final viscosity of the water flooding composition. In some embodiments, the water flooding composition may be considered to be injectable if the final viscosity of the water flooding composition is greater than ninety percent of the initial viscosity of the water flooding composition.

[0035] The thickening polymer may have an initial concentration in the water flooding composition at the upstream end of the permeable test medium and a final concentration in the water flooding composition at the downstream end of the permeable test medium. In some embodiments, the injectability of the water flooding composition may be evaluated having regard to the initial concentration of the thickening polymer and the final concentration of the thickening polymer. In some embodiments, the water flooding composition may be considered to be injectable if the final concentration of the thickening polymer in the water flooding composition is greater than ninety percent of the initial concentration of the thickening polymer in the water flooding composition.

[0036] In some embodiments, the properties of the permeable test medium may be selected to provide a reasonable simulation of the properties of the subterranean formation in which the water flooding composition may be used and/or may be selected so that they may be correlated with the properties of the subterranean formation empirically or in some other manner.

[0037] In some embodiments, the permeable test medium may have specific dimensions and/or properties. For example, in some embodiments, the permeable test medium

may have an initial permeability of less than 10 darcies. For example, in some embodiments, the permeable test medium may have a length between the upstream end and the downstream end of about ten centimeters.

[0038] As indicated, the water flooding compositions of the invention are formulated to have a viscosity and/or mobility which is compatible with the viscosity and/or mobility of the hydrocarbon deposit which is intended to be produced using the water flooding method, and are formulated to be injectable into the subterranean formation in which the water flooding method is to be performed.

[0039] The formulation of the water flooding compositions to achieve compatibility with the hydrocarbon deposit and injectability into the subterranean formation has been determined to be dependent upon one or more of the molecular weight of the hydroxyethyl cellulose backbone polymer, the composition of the hydrophobic modifier, the substitution level of the hydrophobic modifier in the thickening polymer, and the concentration of the thickening polymer in the water flooding composition.

[0040] It has been observed that the viscosity of a water flooding composition according to the invention tends to increase and the mobility of a water flooding composition tends to decrease as the molecular weight of the hydroxyethyl cellulose backbone polymer increases. It has also been observed that the injectability of a water flooding composition according to the invention does not appear to depend significantly upon the molecular weight of the hydroxyethyl cellulose backbone polymer.

[0041] It has been observed that the viscosity of a water flooding composition according to the invention tends to increase and the mobility of a water flooding composition tends to decrease as the number of unsubstituted carbon atoms in the hydrophobic modifier increases. It has also been observed that the injectability of a water flooding composition according to the invention tends to decrease as the number of unsubstituted carbon atoms in the hydrophobic modifier increases.

[0042] It has been observed that the viscosity of a water flooding composition according to the invention tends to increase and the mobility of a water flooding composition tends to decrease as the substitution level of the hydrophobic modifier in the thickening polymer increases. It has also been observed that the injectability of a water flooding composition according to the invention tends to decrease as the substitution level of the hydrophobic modifier in the thickening polymer increases.

[0043] It has been observed that the viscosity of a water flooding composition according to the invention tends to increase and the mobility of a water flooding composition tends to decrease as the concentration of the thickening polymer in the water flooding composition increases. It has also been observed that the injectability of a water flooding composition according to the invention tends to decrease as the concentration of the thickening polymer in the water flooding composition increases.

[0044] The presence of substances other than water and the thickening polymer in the water flooding compositions of the invention may also affect the mobility of the water flooding compositions and their injectability. By way of non-limiting examples, the water in the water flooding compositions of the invention may be present in brine form and/or as hard brine.

[0045] It has been observed that the viscosity of a water flooding composition according to the invention tends to be

higher and the mobility of a water flooding composition according to the invention tends to be lower if the water in the water flooding composition is present in brine form and/or as hard brine than if the water in the water flooding composition is relatively pure. This phenomenon is believed to be attributable to the enhancement of intramolecular and intermolecular association of the thickening polymers of the invention (as described below), due to the presence of ions in the water of the water flooding composition.

[0046] The thickening polymers of the invention may be described generally as cellulosic associating polymers. In such polymers, viscosity/mobility and injectability are believed to be dependent upon at least two different mechanisms of action. A first mechanism of action is “entanglement”, which is believed to be attributable primarily to the molecular weight of the backbone polymer and which increases as the molecular weight (and thus the length) of the backbone polymer increases.

[0047] A second mechanism of action is “association”, which is attributable to the presence and hydrophobicity of the hydrophobic modifier. Without intending to be bound by theory, it is believed that the hydrophobic modifier groups interact or “associate”, both within a single molecule of a thickening polymer and between adjacent molecules of a thickening polymer.

[0048] The degree of association of a water flooding composition according to the invention increases as the number of unsubstituted carbon atoms provided by the hydrophobic modifier increases. Increasing the number of unsubstituted carbon atoms may be achieved by increasing the “size” of the hydrophobic modifier, by increasing the substitution level of the hydrophobic modifier in the thickening polymer, and/or by increasing the concentration of the thickening polymer in the water flooding composition. As the degree of association increases, the viscosity of a water flooding composition increases, the mobility of the water flooding composition decreases, and the injectability of the water flooding composition decreases.

[0049] As noted above, the molecular weight of the hydroxyethyl cellulose backbone polymer does not appear to significantly affect the injectability of the water flooding composition.

[0050] As a result, it would appear that while the viscosity and mobility of a water flooding composition according to the invention is dependent upon both the molecular weight of the hydroxyethyl cellulose backbone polymer and upon the degree of association of the water flooding composition, the injectability of a water flooding composition according to the invention is dependent primarily upon the degree of association of the water flooding composition.

[0051] These phenomena facilitate the formulation of the water flooding compositions of the invention which provide an appropriate viscosity and/or mobility of the water flooding compositions while maintaining injectability of the water flooding compositions.

[0052] For example, in comparison with the teachings of U.S. Pat. No. 4,529,523 (Landoll), the water flooding compositions of the invention utilize relatively higher molecular weight backbone polymers having a molecular weight of between 1,000,000 and 2,000,000 (in stark contrast with the molecular weight range of 50,000 to 1,000,000 specified in Landoll) to increase the viscosity and reduce the mobility of the water flooding composition, while utilizing a modest degree of association derived from the hydrophobic modifier

to provide the beneficial effects of the presence of the hydrophobic modifier without unduly compromising the injectability of the water flooding composition.

[0053] As a result of the above, in some embodiments, the invention relates to a method of secondary hydrocarbon recovery of a type which comprises passing a water flooding composition through a subterranean formation containing a hydrocarbon deposit, in which the method is characterized by the water flooding composition being comprised of water and a thickening polymer, the thickening polymer having a concentration of between about 0.01 percent and about 1 percent by weight of the water flooding composition, the thickening polymer comprising:

[0054] (a) a hydroxyethyl cellulose backbone polymer having a molecular weight of between about 1,000,000 and about 2,000,000; and

[0055] (b) a hydrophobic modifier in a substitution level in the thickening polymer of between about 0.1 percent and about 2 percent by weight of the thickening polymer, wherein the hydrophobic modifier is comprised of an alkyl hydrocarbon based material containing between about 10 and about 24 unsubstituted carbon atoms per group;

wherein the water flooding composition is formulated to have a viscosity of between 2 mPa·s and 100 mPa·s and to be injectable into the subterranean formation.

[0056] As a result of the above, in some embodiments, the invention relates to a method of preparing a water flooding composition for use in a method of secondary hydrocarbon recovery of a type which comprises passing the water flooding composition through a subterranean formation containing a hydrocarbon deposit, the method comprising:

[0057] (a) selecting a hydroxyethyl cellulose backbone polymer having a molecular weight of between 1,000,000 and 2,000,000;

[0058] (b) selecting a hydrophobic modifier comprised of an alkyl hydrocarbon based material containing between 10 and 24 unsubstituted carbon atoms per group;

[0059] (c) providing a thickening polymer comprising the hydroxyethyl cellulose backbone polymer and the hydrophobic modifier in a substitution level in the thickening polymer of between 0.1 percent and 2 percent by weight of the thickening polymer; and

[0060] (d) combining the thickening polymer with water to provide the water flooding composition, wherein the thickening polymer has a concentration of between 0.1 percent and 1 percent by weight of the water flooding composition;

wherein the water flooding composition has a viscosity of between 2 mPa·s and 100 mPa·s and is injectable into the subterranean formation.

[0061] In some embodiments, the molecular weight of the hydroxyethyl cellulose backbone polymer may be about 1,300,000.

[0062] In some embodiments, the concentration of the thickening polymer in the water flooding composition may be between about 0.05 percent and 0.25 percent by weight of the water flooding composition. In some embodiments, the concentration of the thickening polymer in the water flooding composition may be between about 0.05 percent and about 0.2 percent by weight. In some embodiments, the concentration of the thickening polymer in the water flooding composition may be about 0.2 percent.

[0063] In some embodiments, the alkyl hydrocarbon based material of the hydrophobic modifier may contain between about 12 and about 18 unsubstituted carbon atoms per group. In some embodiments, the alkyl hydrocarbon based material of the hydrophobic modifier may be comprised of a plurality of materials. In some embodiments, the alkyl hydrocarbon based material of the hydrophobic modifier may be comprised of dodecyl tetradecyl glycidyl ether.

[0064] As used herein, the substitution level of the hydrophobic modifier in the thickening polymer may be calculated by acetylating hydroxyl groups in the thickening polymer with acetic anhydride, analyzing the reaction products using proton nuclear magnetic resonance (proton NMR or $^1\text{H NMR}$) techniques, and integrating the acetyl CH_3 and hydrophobic modifier CH_2 peaks from the NMR spectra. The ratio of these two peaks indicates the level of substitution of the hydrophobic modifier in the thickening polymer. Higher molecular weight thickening polymers may be partially hydrolyzed by sonication prior to acetylation in order to reduce their molecular weights and their ultimate viscosity in deuterated chloroform (CDCl_3) for the NMR analysis.

[0065] In some embodiments, the substitution level of the hydrophobic modifier in the thickening polymer may be between about 0.1 percent and about 1.5 percent by weight of the thickening polymer. In some embodiments, the substitution level of the hydrophobic modifier in the thickening polymer may be between about 0.4 percent and about 1.2 percent by weight of the thickening polymer. In some embodiments, the substitution level of the hydrophobic modifier in the thickening polymer may be between about 0.7 percent and about 1.2 percent by weight of the thickening polymer.

[0066] In some embodiments, the water of the water flooding composition may be comprised of a brine solution. In some embodiments, the brine solution may be comprised of sodium chloride. In some particular embodiments, the concentration of the brine solution may be about 1% by weight of the brine solution.

[0067] In a particular embodiment, the molecular weight of the hydroxyethyl cellulose backbone polymer may be about 1,300,000, the alkyl hydrocarbon based material of the hydrophobic modifier may be comprised of dodecyl tetradecyl glycidyl ether, the substitution level of the hydrophobic modifier may be between about 0.7 percent and about 1 percent by weight of the thickening polymer, and the concentration of the thickening polymer in the water flooding composition may be about 0.2 percent by weight of the water flooding composition. In the particular embodiment, the water of the water flooding composition may be comprised of a brine solution. In the particular embodiment, the brine solution may be comprised of 1% sodium chloride by weight of the brine solution.

BRIEF DESCRIPTION OF DRAWINGS

[0068] Embodiments of the invention will now be described with reference to the accompanying drawings, in which:

[0069] FIG. 1 is a table summarizing the compositions and properties of various thickening polymers and water flooding compositions.

[0070] FIG. 2 is a table summarizing filtration test results for the water flooding compositions in FIG. 1, for filtration through both a Whatman #1 filter and a sandpack.

[0071] FIG. 3 is a table summarizing the properties of sandpack cores which were used to conduct coreflood tests for selected water flooding compositions from FIG. 1.

[0072] FIG. 4 is a table summarizing the properties of the oil which was used to perform coreflood tests for selected water flooding compositions from FIG. 1.

[0073] FIG. 5 is a table summarizing results of coreflood tests conducted using selected water flooding compositions from FIG. 1.

[0074] FIG. 6 is a schematic drawing of the apparatus used to conduct the sandpack filtration tests which are summarized in FIG. 2.

[0075] FIG. 7 is a schematic drawing of the apparatus used to conduct the coreflood tests which are summarized in FIG. 5.

[0076] FIG. 8 is a graph depicting data obtained from coreflood tests comparing injection pressure in kPa as a function of throughput in pore volumes (PV) for the HPAM and HMHEC 1206 water flooding compositions from FIG. 1.

[0077] FIG. 9 is a graph depicting data obtained from coreflood tests comparing injection pressure in kPa as a function of throughput in pore volumes (PV) for the HPAM and HMHEC 0603 water flooding compositions from FIG. 1.

[0078] FIG. 10 is a graph depicting data obtained from coreflood tests comparing oil recovery as a percentage of original oil in place (OOIP) as a function of throughput in pore volumes (PV) for the HPAM, HMHEC 1206 and HMHEC 0603 water flooding compositions from FIG. 1.

[0079] FIG. 11 is a graph depicting data obtained from sandpack filtration tests comparing effective viscosity in the sandpack in $\text{mPa}\cdot\text{s}$ as a function of linear velocity in feet per day for selected water flooding compositions from FIG. 1, in which the aqueous component of the water flooding compositions is comprised of 1% NaCl.

[0080] FIG. 12 is a graph depicting data obtained from sandpack filtration tests comparing effective viscosity in the sandpack in $\text{mPa}\cdot\text{s}$ as a function of linear velocity in feet per day for selected water flooding compositions from FIG. 1, in which the aqueous component of the water flooding compositions is comprised of either 1% NaCl or hard brine.

DETAILED DESCRIPTION

[0081] The present invention is directed at a method of secondary hydrocarbon recovery of a type which comprises passing a water flooding composition through a subterranean formation containing a hydrocarbon deposit. One purpose of passing the water flooding composition through the subterranean formation is to displace the hydrocarbon deposit toward one or more production wellbores which are in fluid communication with the subterranean formation.

[0082] As a result, the method typically involves injecting the water flooding composition into one or more injection wellbores which are in fluid communication with the subterranean formation and which are separated from the production wellbores so that the water flooding composition can displace the hydrocarbon deposit toward the production wellbores as it passes through the subterranean formation.

[0083] The method may further comprise additional steps or procedures which are performed before and/or after the water flooding composition is passed through the subterranean formation.

[0084] The invention is particularly directed at formulations for the water flooding composition which result in the water flooding composition having a viscosity and/or mobil-

ity which is compatible with the viscosity and/or mobility of the hydrocarbon deposit which is intended to be produced from the subterranean formation, and which result in the water flooding composition being injectable into the subterranean formation.

[0085] The water flooding compositions of the invention are comprised of water and a thickening polymer. The thickening polymer is comprised of a hydroxyethyl cellulose backbone polymer and a hydrophobic modifier. The hydrophobic modifier is comprised of an alkyl hydrocarbon based material. The water flooding compositions of the invention may be further comprised of other materials and/or substances.

[0086] The formulations for water flooding compositions of the invention are based upon a number of considerations.

[0087] First, the formulations for water flooding compositions of the invention are based upon a consideration of the hydrocarbon deposit which is intended to be produced from the subterranean formation and upon the mobility of a water flooding composition which must be achieved in order for the mobility of the water flooding composition to be compatible with the mobility of the hydrocarbon deposit.

[0088] Generally, the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is preferably no greater than about 100:1, more preferably no greater than about 50:1, more preferably no greater than about 10:1, or even more preferably no greater than about 2:1.

[0089] For many typical hydrocarbon deposits comprising oil, the viscosity of the water flooding composition is preferably between about 2 mPa·s and about 100 mPa·s, more preferably between about 5 mPa·s and about 50 mPa·s, or even more preferably between about 5 mPa·s and about 40 mPa·s.

[0090] Second, the formulations for water flooding compositions of the invention are based upon a consideration of the properties of the subterranean formation and upon ensuring that a water flooding composition will be injectable into the subterranean formation.

[0091] Generally, a water flooding composition may be considered to be injectable if it can pass through the subterranean formation without causing significant plugging of the subterranean formation.

[0092] A water flooding composition may be assessed for injectability either during performance of the water flooding method or by testing the water flooding composition before it is used in the performance of the water flooding method. In either case, indicia of injectability or lack of injectability may relate to changes in the composition or properties of the water flooding composition and/or the subterranean formation as the water flooding composition is passed therethrough.

[0093] One method for testing a water flooding composition before it is used in the performance of the water flooding method comprises passing the water flooding composition through a permeable test medium.

[0094] One suitable permeable test medium is a sandpack having an upstream end and a downstream end. One suitable test method is a sandpack filtration technique. A sandpack used for the sandpack filtration technique preferably has an initial permeability of less than about 10 darcies so that it is reasonably representative of a subterranean formation. In one test configuration, a sandpack has had an initial permeability of about 3 darcies. In one test configuration, a sandpack has had a length from the upstream end to the downstream end of about ten centimeters.

[0095] The procedure for testing a water flooding composition in a sandpack comprises passing the water flooding composition through the sandpack under constant or varying conditions of pressure and/or flowrate.

[0096] The water flooding composition will exhibit an initial concentration of the thickening polymer at the upstream end of the sandpack and will exhibit a final concentration of the thickening polymer at the downstream end of the sandpack. If the final concentration of the thickening polymer is less than the initial concentration of the thickening polymer, retention of the thickening polymer in the sandpack, potential plugging of the sandpack, and a lack of injectability of the water flooding composition may be indicated.

[0097] Generally, in order for a water flooding composition to be considered injectable in the sandpack test, the final concentration of the thickening polymer in the water flooding composition should be greater than ninety percent of the initial concentration of the thickening polymer in the water flooding composition.

[0098] The water flooding composition will exhibit an initial viscosity at the upstream end of the sandpack and will exhibit a final viscosity at the downstream end of the sandpack. If the final viscosity is less than the initial viscosity, retention of the thickening polymer in the sandpack, potential plugging of the sandpack, and a lack of injectability of the water flooding composition may be indicated.

[0099] Generally, in order for a water flooding composition to be considered injectable in the sandpack test, the final viscosity of the water flooding composition should be greater than ninety percent of the initial viscosity of the water flooding composition.

[0100] Third, the formulations for water flooding compositions of the invention are based upon a consideration of the effects of the following variables upon the viscosity/mobility and the injectability of a water flooding composition:

- [0101]** 1. the molecular weight of the hydroxyethyl cellulose backbone polymer;
- [0102]** 2. the composition of the hydrophobic modifier;
- [0103]** 3. the substitution level of the hydrophobic modifier in the thickening polymer; and
- [0104]** 4. the concentration of the thickening polymer in the water flooding composition.

[0105] Fourth, the formulations for water flooding compositions of the invention are based upon a consideration of the salt and/or brine conditions which the water flooding compositions may be exposed to, resulting either from the water from which the water flooding compositions are prepared or from the environment to which the water flooding compositions may be exposed.

[0106] The thickening polymers of the invention may be described generally as cellulosic associating polymers. The formulations for water flooding compositions according to the invention are based upon a consideration of theories relating to the mechanisms of action upon which the viscosity/mobility and injectability of a water flooding composition may be dependent.

[0107] In particular these properties of water flooding compositions are believed to be dependent upon "entanglement" as a first mechanism of action and "association" as a second mechanism of action.

[0108] Entanglement is believed to be attributable primarily to the molecular weight of the hydroxyethyl cellulose backbone polymer and appears to affect only the viscosity/mobility of a water flooding composition. The degree of

entanglement increases as the molecular weight of the hydroxyethyl cellulose backbone polymer increases, thereby resulting in an increase in the viscosity and a decrease in the mobility of a water flooding composition.

[0109] Association is believed to be attributable to the presence and hydrophobicity of the hydrophobic modifier and appears to affect both the viscosity/mobility of a water flooding composition and the injectability of a water flooding composition. The degree of association increases as the number of unsubstituted carbon atoms provided by the hydrophobic modifier increases. The number of unsubstituted carbon atoms provided by the hydrophobic modifier may be increased by increasing the “size” of the hydrophobic modifier, by increasing the substitution level of the hydrophobic modifier in the thickening polymer, and/or by increasing the concentration of the thickening polymer in the water flooding composition.

[0110] The goal in formulating the water flooding compositions of the invention is to increase the viscosity and thus reduce the mobility of the water flooding composition so that the viscosity/mobility is compatible with the hydrocarbon deposit, while simultaneously maintaining an acceptable injectability of the water flooding composition in the subterranean formation.

[0111] As noted above, an increase in viscosity/reduction in mobility of a water flooding composition can be achieved by increasing entanglement of the thickening polymer and/or by increasing the degree of association of the water flooding composition. However, increasing viscosity/reducing mobility of the water flooding composition by increasing the degree of association of the water flooding composition will simultaneously result in a decrease in the injectability of the water flooding composition. Increasing the viscosity/reducing mobility of the water flooding composition by increasing the entanglement of the thickening polymer appears to have no significant effect upon the injectability of the water flooding composition.

[0112] As a result, a target viscosity/mobility of a water flooding composition can be achieved by a combination of the effects of entanglement and association. As the degree of entanglement increases, the degree of association may decrease in order to achieve the target viscosity/mobility. Conversely, as the degree of entanglement decreases, the degree of association must increase in order to achieve the target viscosity/mobility.

[0113] However, each particular hydrophobic modifier will exhibit a maximum degree of association, above which the water flooding composition will not be injectable. More particularly, for any particular hydrophobic modifier, increasing the substitution level of the hydrophobic modifier in the thickening polymer and/or increasing the concentration of the thickening polymer in the water flooding composition beyond an association limit will result in the water flooding composition not being injectable.

[0114] As a result, the association limit of each particular hydrophobic modifier will determine the minimum amount of entanglement (i.e., the minimum molecular weight of the hydroxyethyl cellulose backbone polymer) which is required for achieving the target viscosity/mobility for the water flooding composition while simultaneously maintaining the injectability of the water flooding composition.

[0115] Fifth, the formulations for water flooding compositions of the invention are based upon considerations of cost

and availability for different hydroxyethyl cellulose backbone polymer candidates and different hydrophobic modifier candidates.

[0116] Other or additional considerations may apply in particular circumstances involving the practice of the invention.

[0117] Having regard to the considerations outlined above, it has been determined that the range of molecular weights for hydroxyethyl cellulose backbone polymers which are suitable for use in the invention is between about 1,000,000 and about 2,000,000.

[0118] If the molecular weight of the hydroxyethyl cellulose backbone polymer is less than about 1,000,000, the degree of association for the hydrophobic modifier which is required to achieve a viscosity/mobility which is compatible with the hydrocarbon deposit may result in a water flooding composition which is not injectable.

[0119] As the molecular weight of the hydroxyethyl cellulose backbone polymer increases from 1,000,000 and approaches 2,000,000, the backbone polymer may become more difficult to obtain and the cost of the backbone polymer may become prohibitive. As a result, the practical upper limit of the molecular weight of the hydroxyethyl cellulose backbone polymer may be less than 2,000,000. In some embodiments, depending upon availability and cost, the preferred upper limit of the molecular weight of the hydroxyethyl cellulose backbone polymer may be about 1,500,000.

[0120] The following general guidelines have therefore been established for the formulation of water flooding compositions which may have a viscosity/mobility which is compatible with a hydrocarbon deposit and which may be injectable into a subterranean formation:

[0121] (a) the hydroxyethyl cellulose backbone polymer has a molecular weight of between about 1,000,000 and about 2,000,000;

[0122] (b) the hydrophobic modifier is comprised of an alkyl hydrocarbon based material containing between about 10 and about 24 unsubstituted carbon atoms per group, or more preferably between about 12 and about 18 unsubstituted carbon atoms per group;

[0123] (c) the substitution level of the hydrophobic modifier in the thickening polymer is between about 0.1 percent and about 2 percent by weight of the thickening polymer, or preferably between about 0.1 percent and about 1.5 percent by weight of the thickening polymer, or even more preferably between about 0.4 percent and about 1.2 percent by weight of the thickening polymer, or even more preferably between about 0.7 percent and about 1.2 percent by weight of the thickening polymer; and

[0124] (d) the concentration of the thickening polymer in the water flooding composition is between about 0.01 percent and about 1 percent by weight of the water flooding composition, or more preferably between about 0.05 percent and about 0.25 percent by weight of the water flooding composition.

[0125] The water flooding compositions are preferably formulated within the ranges set out above to achieve a target viscosity of between about 2 mPa·s and about 100 mPa·s, more preferably between about 5 mPa·s and about 50 mPa·s, or even more preferably between about 5 mPa·s and about 40 mPa·s and/or to achieve a ratio of the mobility of the water flooding compositions to the mobility of the hydrocarbon deposit of no greater than about 100:1, more preferably no

greater than about 50:1, more preferably no greater than about 10:1, or even more preferably no greater than about 2:1.

[0126] The water flooding compositions are formulated within the ranges set out above to achieve injectable water flooding compositions, as assessed during performance of the water flooding method or by testing the water flooding compositions before they are used in the water flooding method.

[0127] In many applications of the invention, achieving injectability of the water flooding compositions may follow from formulating the water flooding compositions in accordance with the above ranges and target viscosities. In some applications of the invention, achieving injectability of the water flooding compositions may require some modification of the formulations of the water flooding compositions within the above ranges and target viscosities.

[0128] The thickening polymers of the invention may be prepared by using any suitable method, including the specific methods described in U.S. Pat. No. 4,228,277 (Landoll), in U.S. Pat. No. 4,529,523, and other methods known in the art.

[0129] The water flooding compositions of the invention may be prepared by mixing the thickening polymer with water and with any other suitable materials and/or substances. The water may be present in relatively pure form, in brine form, as hard brine, and/or may contain other substances and/or impurities.

Example 1

Preparation of Thickening Polymers (HMHEC) from Hydroxyethyl Cellulose (HEC)

[0130] A 500 mL round bottom flask was charged with 10 grams of hydroxyethyl cellulose (HEC) having a molecular weight of 1,300,000, followed by 1.25 grams of dodecyl tetradecyl glycidyl ether and 87.5 grams of isopropanol. The flask was then purged with nitrogen gas.

[0131] The flask was fitted with a mechanical stirrer, and 87.5 grams of 1 percent sodium hydroxide (NaOH), pre purged with nitrogen gas was added to the flask while stirring the flask.

[0132] The resulting viscous slurry was purged briefly with nitrogen gas and then stirred for five hours at 60 degrees Celsius. After five hours, 2 grams of acetic acid and 100 milliliters of acetone were added to the flask.

[0133] After 10-15 minutes, the contents of the flask was transferred to a one liter beaker and about 400 milliliters of acetone was added for precipitation with stirring.

[0134] The resulting material was centrifuged and washed twice with 100 milliliter acetone washings. After air drying, 180 milliliters of water was added with stirring, yielding a gel. An additional 40 milliliters of water was added and mixed with a spatula immediately prior to transfer of the material to a dialysis tube. The removal of the sodium acetate salt was confirmed using Fourier transform infrared spectroscopy (FTIR).

[0135] The material was then freeze-dried and ground to yield 9 grams of a thickening polymer, consisting of hydrophobically modified hydroxyethyl cellulose (HMHEC) as a fluffy white powder, which thickening polymer was designated as HMHEC 0603.

[0136] A similar synthesis process was used to prepare other HMHEC thickening polymers from HEC having molecular weights of 720,000 or 1,000,000, also using dodecyl tetradecyl glycidyl ether as the hydrophobic modifier. These other HMHEC thickening polymers were designated as indicated in FIG. 1.

Example 2

Preparation of Water Flooding Compositions

[0137] A number of different water flooding compositions were prepared using the HMHEC thickening polymers of Example 1. An additional water flooding composition, designated as HPAM, was prepared using Flopaam™ 3630 as the thickening polymer. Flopaam™ 3630 is a polyacrylamide polymer produced by SNF Group of Andrezieux, France, which is commonly used as a thickening polymer in secondary hydrocarbon recovery.

[0138] The water flooding compositions were prepared from the thickening polymers by mixing the thickening polymers with water. The water was provided as either relatively pure water, as a 1 percent brine (NaCl) solution, or as a hard brine (NaCl) solution containing total dissolved solids of 8.5 percent and a hardness of 0.38 percent.

[0139] The compositions and properties of the HMHEC and HPAM water flooding compositions are summarized in FIG. 1.

[0140] In FIG. 1, it is noted that two different values for viscosity in 1% NaCl are provided for the water flooding compositions containing HMHEC 1206 and HMHEC 0603. The first (and lower) values for viscosity were obtained from the sandpack filtration tests. The second (and higher) values for viscosity were obtained from the coreflood tests. Although the reason for these discrepancies in the data is not known, it is possible that the HMHEC 1206 and HMHEC 0603 water flooding compositions which were used in the sandpack filtration tests may actually have contained a lower concentration of the thickening polymers than the water flooding compositions which were used in the coreflood tests.

Example 3

Water Flooding Compositions—Filtration Tests

[0141] The water flooding compositions of Example 2 and FIG. 1 were filtered using one or both of two filtering techniques, both of which involved passing the water flooding compositions through a permeable test medium.

[0142] The first filtering technique comprised filtering the water flooding compositions through two Whatman #1 (11 μm) filters. A net pressure drop of 100 kPa using compressed air was placed across the filters in order to provide a pressure gradient.

[0143] The viscosities of the water flooding compositions were measured before and after the filtration to obtain an initial viscosity value and a final viscosity value. A reduction in the viscosity of the water flooding composition indicated that all of the thickening polymer did not pass through the filters. It is noted that a similar measurement could have been made of the concentration of the thickening polymer in the water flooding compositions to obtain an initial concentration value and a final concentration value.

[0144] The filterability of the water flooding compositions was also evaluated by the filter ratio, which compares the rate of filtration over different time intervals:

$$\text{Filter Ratio} = \frac{\text{Time to Filter 300 grams} - \text{Time to Filter 200 grams}}{\text{Time to Filter 200 grams} - \text{Time to Filter 100 grams}}$$

[0145] A filter ratio greater than 1 indicated that the permeability of the filter was decreasing over time, suggesting that all of the thickening polymer did not pass through the filter and thus plugged the filter.

[0146] The second filtering technique comprised filtering the water flooding compositions through a compact sandpack filtration test core having a permeability of less than about 10 darcies and a length from an upstream end to a downstream end of about 10 centimeters.

[0147] A schematic drawing of the apparatus which was used to conduct the sandpack filtration tests is provided in FIG. 6.

[0148] Referring to FIG. 6, the filtration test apparatus (20) comprises a filtration test core (22). The filtration test core (22) has an upstream end (24) and a downstream end (26). The upstream end (24) of the filtration test core (22) is in fluid communication with an injection fluid vessel (28). A compressed air source (30) is in fluid communication with the injection fluid vessel (28). The compressed air source (30) provides a means for pressurizing fluid which is contained within the injection fluid vessel (28).

[0149] The downstream end (26) of the filtration test core (22) is in fluid communication with an effluent collection vessel (32). The weight of the effluent collection vessel (32) is measured with a balance scale (34) in order to determine the weight of effluent fluid which exits the downstream end (26) of the filtration test core (22). Data from the balance scale (34) is transferred to a computer (36) for recordation and analysis.

[0150] In the second filtering technique, the propagation of the water flooding compositions through the filtration test core (22) was measured under a series of net pressure drops from 3.5 kPa to 100 kPa. The weight of the effluent water flooding composition exiting the downstream end (26) of the filtration test core (22) was measured by the balance scale (34) and recorded by the computer (36) as a function of time.

[0151] The water flooding compositions were sampled at the upstream end (24) of the filtration test core (22) and evaluated with a rheometer in order to obtain initial viscosity values for the water flooding compositions. The water flooding compositions were sampled at the downstream end (26) of the filtration test core (22) and evaluated with a rheometer in order to obtain final viscosity values for the water flooding compositions.

[0152] As with the first filtering technique, a reduction in the viscosity of the water flooding composition indicated that all of the thickening polymer did not pass through the filtration test core (22). As with the first filtering technique, a similar measurement could have been made of the concentrations of the thickening polymer in the water flooding compositions to obtain an initial concentration value and a final concentration value.

[0153] Results of the filtration tests for both filtering techniques are provided in FIG. 2.

Example 4

Water Flooding Compositions—Coreflood Tests

[0154] Coreflood tests of a selected number of the water flooding compositions were conducted to study the incremental oil recovery resulting from the use of the water flooding compositions over the oil recovery obtained from an initial water flood procedure. In general, the coreflood tests were performed by conducting a brine water flood first to obtain a meaningful water flood recovery value, conducting a water

flood using one of the water flood compositions, and then conducting a second brine water flood as a chaser flood. The aqueous medium for each of the water flooding compositions was 1% NaCl brine.

[0155] A schematic drawing of the apparatus which was used to conduct the coreflood tests is provided in FIG. 7.

[0156] Referring to FIG. 7, the coreflood test apparatus (50) comprises a sandpack coreflood test core (52). The coreflood test core (52) has an upstream end (54) and a downstream end (56). The upstream end (54) of the coreflood test core (52) is in fluid communication with a pump (58) which is connected with a source of brine (60) and a source of water flooding composition (62).

[0157] The downstream end (56) of the coreflood test core (52) is in fluid communication with a backpressure regulator (64). The backpressure regulator (64) has a liquid outlet (66).

[0158] An upstream pressure transducer (72) is connected with the upstream end (54) of the coreflood test core (52). A midstream pressure transducer (74) is connected with the midpoint of the length of the coreflood test core (52).

[0159] The properties of the coreflood test cores (52) for a number of tests are set out in FIG. 3. For the coreflood tests, the length of the coreflood test cores (52) was about 30 centimeters.

[0160] In conducting the coreflood tests, the coreflood test core (52) was first saturated with a 1% brine solution to obtain its brine permeability.

[0161] Oil was then injected into the coreflood test core (52) to displace mobile water until a constant pressure drop across the coreflood test core (52) was obtained and water production stopped. Properties of the oil are set out in FIG. 4.

[0162] The oil permeability of the coreflood test core (52) was then measured. The coreflood tests were carried out under net overburden pressure of 7000 kPa at a constant core temperature of 20 degrees Celsius.

[0163] The initial brine water flood was conducted by injecting a 1% brine (NaCl) solution into the upstream end (54) of the coreflood test core (52) at a constant flow rate of 3.6 ml/hr. This flow rate equates to a linear velocity of 0.6 feet per day, which is believed to be representative of the flow rates which may be expected in typical reservoirs far removed from a wellbore. Effluent samples were collected at the downstream end (56) of the coreflood test core (52) in a series of pre-weighed tubes at a time interval of 100 minutes. Pressure drops across the coreflood test core (52) generated by the injected brine solution were continuously monitored by the upstream pressure transducer (72) and the midstream pressure transducer (74). The initial brine water flood was continued until about 1 pore volume (PV) had been injected into the coreflood test core (52).

[0164] A water flood composition was then injected continuously into the upstream end (54) of the coreflood test core (52) until at least 2 pore volumes (PV) of the water flood composition had been injected into the coreflood test core (52).

[0165] Finally, a second brine water flood was injected into the upstream end (54) of the coreflood test core (52) as a chaser until about 1 pore volume (PV) had been injected into the coreflood test core (52).

[0166] The results of the coreflood tests are summarized in FIG. 5.

Analysis of Filtration Test Results and Coreflood Test Results

[0167] Referring to FIG. 1, it is observed that the viscosity of the HPAM (polyacrylamide) water flooding composition

was very significantly higher when the water flooding composition was prepared using water as the aqueous medium than when 1% brine (NaCl) or hard brine was used as the aqueous medium. In contrast, the viscosity of the HMHEC water flooding compositions was generally higher when the water flooding compositions were prepared using 1% brine (NaCl) or hard brine as the aqueous medium than when water was used as the aqueous medium. This phenomenon suggests that HMHEC water flooding compositions may exhibit superior durability for use in secondary oil recovery in brine environments than polyacrylamide water flooding compositions.

[0168] Also referring to FIG. 1, it is observed that HMHEC water flooding compositions prepared using a relatively high molecular weight HEC backbone polymer (i.e., 1,300,000) tend to exhibit relatively high viscosity at relatively lower hydrophobe substitution levels than do HMHEC water flooding compositions which are prepared using a relatively low molecular weight HEC backbone polymer (i.e., 720,000). This phenomenon demonstrates that the use of relatively higher molecular weight HEC backbone polymers can be effective to achieve suitably high viscosities at relatively lower levels of substitution (and thus lower degrees of association).

[0169] Also referring to FIG. 1, it is observed that qualitatively, the best overall results with respect to injectability and oil recovery were achieved using either the HPAM water flooding composition or the HMHEC 0603 water flooding composition, suggesting that relatively higher molecular weight HEC backbone polymers with a modest level of hydrophobe substitution can be used to overcome injectability problems which may result from the use of relatively lower molecular weight HEC backbone polymers with a higher level of hydrophobe substitution.

[0170] Referring to FIG. 2, it is observed in the sandpack filtration tests that the HMHEC 0603 water flooding compositions exhibited a very stable and consistent viscosity pre-injection and following injection of two pore volumes, indicating that HMHEC 0603 water flooding compositions can be considered to satisfy the requirement of injectability.

[0171] Referring to FIG. 5, it is observed in the coreflood tests that the HMHEC 0603 water flooding composition exhibited the highest oil recovery (slightly higher than the HPAM water flooding composition) while the HMHEC 1206 water flooding composition exhibited a much lower oil recovery. Furthermore, both the HPAM water flooding composition and the HMHEC 0603 maintained a stable and consistent viscosity pre-injection and post-injection, while the HMHEC 1206 water flooding composition exhibited a dramatic decrease in viscosity from pre-injection to post-injection. This phenomenon suggests that an HMHEC water flooding composition containing a relatively high molecular weight backbone polymer, such as HMHEC 0603 can provide secondary oil recovery results which are comparable to a polyacrylamide (HPAM) water flooding composition.

[0172] Referring to FIG. 8, it is observed that a water flooding composition containing a relatively low molecular weight backbone polymer, such as HMHEC 1206 may exhibit a continuous increase in required injection pressure during a water flooding procedure, while a polyacrylamide (HPAM) water flooding composition may exhibit a relatively stable and consistent required injection pressure during a water flooding procedure.

[0173] Referring to FIG. 9, it is observed that a water flooding composition containing a relatively high molecular weight backbone polymer, such as HMHEC 0603 may exhibit a required injection pressure during a water flooding

procedure which is comparable to that exhibited by a polyacrylamide (HPAM) water flooding composition.

[0174] Referring to FIG. 10, it is observed that a water flooding composition containing a relatively high molecular weight backbone polymer, such as HMHEC 0603 may exhibit an oil recovery during a water flooding procedure which is comparable to that exhibited by a polyacrylamide (HPAM) water flooding composition, while a water flooding composition containing a relatively low molecular weight backbone polymer, such as HMHEC 1206 may exhibit a significantly lower oil recovery during a water flooding procedure.

[0175] Referring to FIG. 11, it is observed that for water flooding compositions in which the aqueous medium was comprised of 1% NaCl, a polyacrylamide (HPAM) water flooding composition exhibited increased effective viscosity in the sandpack filtration tests as the flow rate increased. An explanation for this result is that the transportation of polymer solutions in porous media is affected by both shear and elongational viscosities. In the case of the HPAM water flooding composition, its elongational viscosity increased greatly at high flow rates, leading to higher effective viscosities. Referring also to FIG. 10, it is observed that for water flooding compositions in which the aqueous medium was comprised of 1% NaCl, HMHEC water flooding compositions tended to exhibit a relatively stable and consistent effective viscosity in the sandpack filtration tests within the range of flow rates that was studied.

[0176] Referring to FIG. 12, it is observed that water flooding compositions containing a moderately high to high molecular weight backbone HEC polymer (HMHEC 0318 and HMHEC 0603) wherein the aqueous medium was comprised of a hard brine solution exhibited higher effective viscosities in the sandpack filtration tests at relatively low concentrations of the thickening polymer (i.e., less than 2000 ppm) than did water flooding compositions comprising HMHEC 0318 or HMHEC 0603 at relatively higher concentrations of the thickening polymer (i.e., 2000 ppm) wherein the aqueous medium was comprised of 1% NaCl.

[0177] In summary, an HMHEC water flooding composition containing a relatively high molecular weight backbone polymer (i.e., at least about 1,000,000) and a moderate level of substitution of the hydrophobic modifier may be capable of providing performance in water flooding applications which is comparable to the performance of an HPAM (polyacrylamide) water flooding composition with respect to injectability and oil recovery, and which may be superior to the performance of an HPAM (polyacrylamide) water flooding composition with respect to durability in the presence of a brine environment.

[0178] In this document, the word "comprising" is used in its non-limiting sense to mean that items following the word are included, but items not specifically mentioned are not excluded. A reference to an element by the indefinite article "a" does not exclude the possibility that more than one of the elements is present, unless the context clearly requires that there be one and only one of the elements.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a method of secondary hydrocarbon recovery of a type which comprises passing a water flooding composition through a subterranean formation containing a hydrocarbon deposit, the method characterized by the water flooding composition being comprised of water and a thickening polymer, the thickening polymer having a concentration of between 0.01 percent and 1 percent by weight of the water flooding composition, the thickening polymer comprising:

- (a) a hydroxyethyl cellulose backbone polymer having a molecular weight of between 1,000,000 and 2,000,000; and
- (b) a hydrophobic modifier in a substitution level in the thickening polymer of between 0.1 percent and 2 percent by weight of the thickening polymer, wherein the hydrophobic modifier is comprised of an alkyl hydrocarbon based material containing between 10 and 24 unsubstituted carbon atoms per group;

wherein the water flooding composition is formulated to have a viscosity of between 2 mPa·s and 100 mPa·s and to be injectable into the subterranean formation.

2. The method as claimed in claim 1 wherein the concentration of the thickening polymer in the water flooding composition is between 0.05 percent and 0.25 percent by weight of the water flooding composition.

3. The method as claimed in claim 2 wherein the alkyl hydrocarbon based material of the hydrophobic modifier contains between 12 and 18 unsubstituted carbon atoms per group.

4. The method as claimed in claim 3 wherein the substitution level of the hydrophobic modifier in the thickening polymer is between 0.1 percent and 1.5 percent by weight of the thickening polymer.

5. The method as claimed in claim 4 wherein the hydrocarbon deposit has a mobility, wherein the water flooding composition has a mobility, and wherein a ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 100:1.

6. The method as claimed in claim 5 wherein the water flooding composition is adapted to be capable of being passed through a permeable test medium from an upstream end of the permeable test medium to a downstream end of the permeable test medium, wherein the permeable test medium has an initial permeability of less than 10 darcies, such that the thickening polymer has an initial concentration in the water flooding composition at the upstream end of the permeable test medium and a final concentration in the water flooding composition at the downstream end of the permeable test medium, and such that the final concentration of the thickening polymer in the water flooding composition is greater than ninety percent of the initial concentration of the thickening polymer in the water flooding composition.

7. The method as claimed in claim 6 wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 50:1.

8. The method as claimed in claim 7 wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 10:1.

9. The method as claimed in claim 8 wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 2:1.

10. The method as claimed in claim 5 wherein the water flooding composition is adapted to be capable of being passed through a permeable test medium from an upstream end of the permeable test medium to a downstream end of the permeable test medium, wherein the permeable test medium has an initial permeability of less than 10 darcies, such that the water flooding composition has an initial viscosity at the upstream end of the permeable test medium and a final viscosity at the downstream end of the permeable test medium, and such that the final viscosity of the water flooding composition is greater than ninety percent of the initial viscosity of the water flooding composition.

11. The method as claimed in claim 10 wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 50:1.

12. The method as claimed in claim 11 wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 10:1.

13. The method as claimed in claim 12 wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 2:1.

14. The method as claimed in claim 4 wherein the water flooding composition is adapted to be capable of being passed through a permeable test medium from an upstream end of the permeable test medium to a downstream end of the permeable test medium, wherein the permeable test medium has an initial permeability of less than 10 darcies, such that the thickening polymer has an initial concentration in the water flooding composition at the upstream end of the permeable test medium and a final concentration in the water flooding composition at the downstream end of the permeable test medium, and such that the final concentration of the thickening polymer in the water flooding composition is greater than ninety percent of the initial concentration of the thickening polymer in the water flooding composition.

15. The method as claimed in claim 14 wherein the water flooding composition has a viscosity of between 2 mPa·s and 50 mPa·s.

16. The method as claimed in claim 4 wherein the water flooding composition is adapted to be capable of being passed through a permeable test medium from an upstream end of the permeable test medium to a downstream end of the permeable test medium, wherein the permeable test medium has an initial permeability of less than 10 darcies, such that the water flooding composition has an initial viscosity at the upstream end of the permeable test medium and a final viscosity at the downstream end of the permeable test medium, and such that the final viscosity of the water flooding composition is greater than ninety percent of the initial viscosity of the water flooding composition.

17. The method as claimed in claim 16 wherein the water flooding composition has a viscosity of between 2 mPa·s and 50 mPa·s.

18. The method as claimed in claim 4 wherein the hydroxyethyl cellulose backbone polymer of the water flooding composition has a molecular weight of 1,300,000.

19. The method as claimed in claim 18 wherein the hydrocarbon deposit has a mobility, wherein the water flooding composition has a mobility, and wherein a ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 100:1.

20. The method as claimed in claim 19 wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 50:1.

21. The method as claimed in claim 20 wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 10:1.

22. The method as claimed in claim 21 wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 2:1.

23. The method as claimed in claim 18 wherein the water flooding composition has a viscosity of between 2 mPa·s and 50 mPa·s.

24. The method as claimed in claim 4 wherein the alkyl hydrocarbon based material of the hydrophobic modifier is comprised of dodecyl tetradecyl glycidyl ether.

25. The method as claimed in claim **24** wherein the hydrocarbon deposit has a mobility, wherein the water flooding composition has a mobility, and wherein a ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 100:1.

26. The method as claimed in claim **25** wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 50:1.

27. The method as claimed in claim **26** wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 10:1.

28. The method as claimed in claim **27** wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 2:1.

29. The method as claimed in claim **24** wherein the water flooding composition has a viscosity of between 2 mPa·s and 50 mPa·s.

30. The method as claimed in claim **4** wherein the substitution level of the hydrophobic modifier in the thickening polymer is between 0.7 percent and 1 percent by weight of the thickening polymer.

31. The method as claimed in claim **30** wherein the hydrocarbon deposit has a mobility, wherein the water flooding composition has a mobility, and wherein a ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 100:1.

32. The method as claimed in claim **31** wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 50:1.

33. The method as claimed in claim **32** wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 10:1.

34. The method as claimed in claim **33** wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 2:1.

35. The method as claimed in claim **30** wherein the water flooding composition has a viscosity of between 2 mPa·s and 50 mPa·s.

36. The method as claimed in claim **4** wherein the concentration of the thickening polymer in the water flooding composition is 0.2 percent by weight of the water flooding composition.

37. The method as claimed in claim **36** wherein the hydrocarbon deposit has a mobility, wherein the water flooding composition has a mobility, and wherein a ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 100:1.

38. The method as claimed in claim **37** wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 50:1.

39. The method as claimed in claim **38** wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 10:1.

40. The method as claimed in claim **39** wherein the ratio of the mobility of the water flooding composition to the mobility of the hydrocarbon deposit is no greater than 2:1.

41. The method as claimed in claim **36** wherein the water flooding composition has a viscosity of between 2 mPa·s and 50 mPa·s.

42. The method as claimed in claim **4** wherein the hydroxyethyl cellulose backbone polymer of the water flooding composition has a molecular weight of 1,300,000, wherein the alkyl hydrocarbon based material of the hydrophobic modifier is comprised of dodecyl tetradecyl glycidyl ether, wherein the substitution level of the hydrophobic modifier in the thickening polymer is between 0.7 percent and 1 percent by weight of the thickening polymer, and wherein the concentration of the thickening polymer in the water flooding composition is 0.2 percent by weight of the water flooding composition.

43. The method as claimed in claim **42** wherein the water of the water flooding composition is comprised of a brine solution.

44. The method as claimed in claim **43** wherein the brine solution is comprised of one percent sodium chloride by weight of the brine solution.

45. A method of preparing a water flooding composition for use in a method of secondary hydrocarbon recovery of a type which comprises passing the water flooding composition through a subterranean formation containing a hydrocarbon deposit, the method comprising:

- (a) selecting a hydroxyethyl cellulose backbone polymer having a molecular weight of between 1,000,000 and 2,000,000;
- (b) selecting a hydrophobic modifier comprised of an alkyl hydrocarbon based material containing between 10 and 24 unsubstituted carbon atoms per group;
- (c) providing a thickening polymer comprising the hydroxyethyl cellulose backbone polymer and the hydrophobic modifier in a substitution level in the thickening polymer of between 0.1 percent and 2 percent by weight of the thickening polymer; and
- (d) combining the thickening polymer with water to provide the water flooding composition, wherein the thickening polymer has a concentration of between 0.1 percent and 1 percent by weight of the water flooding composition;

wherein the water flooding composition has a viscosity of between 2 mPa·s and 100 mPa·s and is injectable into the subterranean formation.

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