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(71) Applicant (for CA only): **SCHLUMBERGER CANADA LIMITED** [CA/CA]; 525-3rd Avenue S.W., Calgary, Alberta T2P 0G4 (CA).

(71) Applicant (for FR only): **SERVICES PETROLIERS SCHLUMBERGER** [FR/FR]; 42 rue Saint Dominique, F-75007 Paris (FR).

(71) Applicant (for GB, JP, NL only): **SCHLUMBERGER HOLDINGS LIMITED**; Craigmuir Chambers, Road Town, P.O. Box 71, Tortola (VG).

(71) Applicant (for AL, AM, AU, AZ, BE, BG, BJ, BY, CF, CG, CI, CM, CO, CZ, DE, DK, GA, GN, GQ, GR, GW, HU, ID,

IE, IL, IT, KG, KP, KR, KZ, LT, MD, ML, MR, MX, NE, NO, NZ, OM, PL, RO, RU, SI, SK, SN, TD, TG, TJ, TM, TN, TR, TT, UZ, ZA only): **SCHLUMBERGER TECHNOLOGY B.V.** [NL/NL]; Parkstraat 83-89, NL-2514 The Hague (NL).

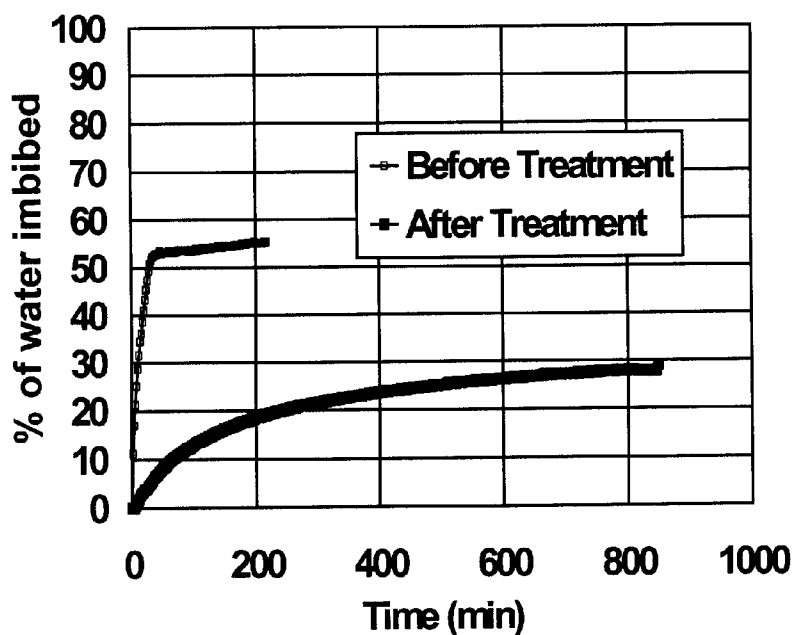
(71) Applicant (for AE, AG, AT, BA, BB, BR, BW, BZ, CH, CN, CR, CU, CY, DM, DZ, EC, EE, EG, ES, FI, GD, GE, GH, GM, HR, IN, IS, KE, KM, KN, LC, LK, LR, LS, LU, LV, LY, MA, MC, MG, MK, MN, MW, MZ, NA, NG, NI, PG, PH, PT, RS, SC, SD, SE, SG, SL, SM, SY, SZ, TZ, UA, UG, VC, VN, ZM, ZW only): **PRAD RESEARCH AND DEVELOPMENT N.V.** [NL/NL]; De Ruyterkade 62, Willemstad (AN).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **PANGA, Mohan K.R.** [IN/US]; Schlumberger Technology Corporation, 100 Schlumberger Drive, MD-1, Sugar Land, TX 77478 (US). **SAMUEL, Mathew** [US/MY]; Schlumberger WTA (M) Sdn Bhd Sdn Bhd, 19th Floor East Wing, Rohas Perkasa, No 8 Jalan Perak, 50450 Kuala Lumpur (MY). **CHAN, Keng Seng** [US/MY]; Schlumberger WTA (M) Sdn Bhd Sdn Bhd, 19th Floor East Wing, Rohas Perkasa, No 8 Jalan Perak, 50450 Kuala Lumpur (MY). **ENKABABIAN,**

[Continued on next page]

(54) Title: PREVENTION OF WATER AND CONDENSATE BLOCKS IN WELLS



(57) Abstract: Compositions and methods are given to prevent, alleviate and remedy water blocks and gas blocks (condensate block or condensate banking). Wettability modifiers are contacted with the formation to change the surfaces from water wet or oil wet to intermediate wet or gas wet. Preferred wettability modifiers include partially or completely fluorinated surfactants or polymers, for example fluorosilanes such as perfluorosilanes, urethane oligomers containing perfluoro alkyl moieties, fluoroacrylates, and fluoroalkyl containing terpolymers or their mixtures. Other examples include surfactants, for example viscoelastic surfactants such as cationic surfactants such as quaternary amines, and zwitterionic surfactants, such as betaines, optionally mixed with co-surfactants.

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Philippe [FR/ID]; P.T. Dowell Anadrill Schlumberger, P.O. Box 117, Jl. Mulawarman Km 20, Kelurahan Manggar, 76117 Balikpapan (ID). **CHENEVIERE, Pascal** [FR/FR]; Total, CST JF, Avenue Larribau, F-64018 Pau Cedex (FR).

(74) **Agent: MITCHELL, Thomas**; 110 Schlumberger Drive, MD-1, Sugar Land, TX 77478 (US).

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PREVENTION OF WATER AND CONDENSATE BLOCKS IN WELLS

Field of the Invention

[0001] The invention relates to the prevention of water blocks and the prevention of condensate banking in oil and gas producing subterranean formations. More particularly, it relates to treating subterranean formations to change the wettability from oil or water wet to intermediate wet or gas wet.

Background of the Invention

[0002] The accumulation of water near the wellbore in an oil or gas well can decrease the productivity by decreasing the relative permeability of oil or gas. The sources for water accumulation could be filtrate water from drilling mud, cross flow of water from water-bearing zones, water from completion or workover operations, water from matrix/fracture treatments, water from emulsions, etc. The problem of productivity decline because of an increase in near wellbore water saturation is known as *water block*.

[0003] In gas wells, in addition to water, liquid hydrocarbons that accumulate near the wellbore can also decrease the productivity of gas. The sources for the accumulation of hydrocarbons could be the use of oil-based drilling mud in drilling operations, hydrocarbon liquids used in workover operations, the use of oil-based fracturing fluids, etc. In addition to such external sources, the liquid hydrocarbons that condense out of the gas phase (called condensates) due to the decline in pressure below the dew point pressure of the gas also hinder the gas production. This phenomenon of condensation with a decrease in pressure is called retrograde condensation. When condensates block the production, the problem is called *condensate block* or *condensate banking*. In this specification, the term condensate banking is used for a decline in gas production due to any liquid hydrocarbons, condensates, or hydrocarbons from external sources such as those mentioned above, for example oil based drilling muds.

[0004] Water blocks and condensate banks can occur together or independently, leading to a decrease in well productivity and in some cases to complete shut down in production. (See, for example, SPE papers 13650, 28479, and 30767.) During the early stages of production, condensate banking occurs close to the wellbore where the pressure first decreases below the dew point pressure. Even for a small amount of condensate drop out (as a fraction of the produced hydrocarbon), significant condensate build-up can occur, as several pore volumes of gas pass through the wellbore. With time, the condensate bank extends deep into the reservoir due to drawdown and depletion of the reservoir pressure. Unlike water blocks, which mainly affect the near wellbore region, condensate banks can affect a region far from the wellbore. Condensate banking is a continuing problem, because the condensate accumulates with time even after an initial cleanup.

[0005] To increase temporarily the production in a well affected by water block or condensate bank the following methods have been employed (see SPE paper 77546): fracturing the well; dry gas injection; and solvent injection (see, for example, SPE papers 62935, 63161, 68683, 80901, and 84216). In fracturing, the purpose is to bypass the zone damaged by water or by condensate blocks and to increase the bottomhole pressure, if possible, above the dew point pressure to decrease the formation of condensate. In dry gas injection, the clean up is by vaporization of condensate into the gas (see, for example, SPE papers 68683 and 71526). In the third method, solvents such as methanol, isopropyl alcohol, and others, are injected into the well. The solvents mix with water or condensate and enhance clean up by reducing the interfacial tension and by increasing the volatility of the liquid.

[0006] The methods described above are remedial, and help in the temporary clean-up of existing water or condensate blocks. If the above-mentioned methods are used, then if the water block or condensate bank problem reoccurs, then the well must be treated again. It would be beneficial to have a more permanent method of preventing water block and gas banking.

Summary of the Invention

[0007] A method has been developed for prevention of water blocks in gas and oil wells and condensate blocks in gas wells using wettability modifiers. This method may

be applied to all oil or gas wells with no water or condensate block problems as a preventive solution. It may also be used as a remedial method for clean-up of most or all of existing water or condensate blocks; after these clean-ups it will act to prevent future water block or condensate blocking in the same location. Alternatively, the chemical system may be mixed with fluids used in fracturing, acidizing, drilling and other workover operations to unload the unwanted oil or water based fluids that enter the formation during the operation. The method may also be used to enhance production in oil wells and injection of water in injector wells because of low near well bore pressure drop resulting from the wettability alteration. The wettability alteration is permanent.

[0008] The application of this method to treating a subterranean formation may involve single or multiple stages, separated into pretreatment, main and post treatment stages. The pretreatment stage may involve injection of a preflush of water or brine, one or more alcohols, one or more of other solvents, one or more clay stabilizers, one or more water-solvent mixtures, or one or more treatment fluids used in such oilfield treatments as matrix stimulation, and other treatments, one or more other fluids, or mixtures of such fluids. In the main stage, the wettability modifier may be dispersed or mixed in a carrier fluid that may be a solvent or water and may be injected into the well. Optionally, the formation may be soaked in the fluid that contains a wettability modifier for a period of time (shut-in period). The soaking may not be necessary for some wettability modifiers, some formations, or some conditions. The wettability modifier adheres to the formation by adsorption, chemical bonding, aggregation, electrostatic attraction, precipitation, aggregation, etc. In a typical post treatment stage the fluid injected in the main stage is displaced immediately after the main stage, or after a shut-in period, using a gas such as N₂, CO₂, etc., or any of the fluids used in the pretreatment stage, or fluids similar to those fluids. This procedure provides better placement of the wettability modifier, and/or enhancement of the flow back of the fluid or fluids injected in the main stage. In this specification, we may occasionally use the term “solvent” or “carrier fluid” for any of the pretreatment main or post treatment fluids. When the well is put into production, or back on production, or used as an injector, the solvent and the left-over wettability modifier flow out of the formation or deeper into the formation, leaving a coating of the wettability modifier in the

formation. This alters the wettability of the formation that is initially water or oil wet to an intermediate or gas wetting condition that reduces the capillary pressure of the formation. During the production life cycle of the well, although it generally will not occur, if any water or condensate accumulate in this wettability altered zone, they may easily be cleaned up, thus preventing the formation of water or condensate blocks and enhancing production.

[0009] The wettability modifiers may include cationic, anionic, or zwitterionic surfactants, or polymers containing chemical groups or moieties that have a tendency to repel oil or water. For example, the presence of fluorine in the surfactant or polymer may give both hydrophobic and oleophobic nature to the chemical. Preferred wettability modifiers include partially or completely fluorinated surfactants or polymers, for example fluorosilanes such as perfluorosilanes, urethane oligomers containing perfluoro alkyl moieties, fluoroacrylates, and fluoroalkyl containing terpolymers. Other examples include surfactants, such as cationic, zwitterionic, anionic, and nonionic surfactants.

[0010] The wettability modifier may be introduced in solution, for example in water, brine, an alcohol such as methanol, isopropyl alcohol, etc., a ketone, an ether, an ester, hydrocarbons such as petroleum distillates, diesel, biodiesel, or their derivatives, or a mixture of these solvents.

[0011] Since this is a preventive or remediative treatment, the fluids injected into the formation should not create an additional water or condensate block. Thus, the carrier fluid for the chemicals may optionally contain solvents that are volatile (e.g.: alcohol-based solvents) or have low interfacial tension with the gas phase (low capillary pressure) so that, when the well is put on production, the fluid flows out of the formation or deeper into the formation either because of displacement by the gas or evaporation into the gas phase because of high volatility. Since the wettability modifier is adhering to the formation and cannot easily be removed by the flow of fluids or gas, this composition and method provides a long-term solution for the prevention of water/condensate blocks.

Brief Description of the Drawings

[0012] Figure 1 shows the contact angle θ of water when placed on a solid surface.

[0013] Figure 2 shows the experimental set-up for the imbibition test.

[0014] Figure 3 shows imbibition data for a fluorocarbon wettability modifier of the Invention, before and after treatment.

[0015] Figure 4 shows imbibition data with another fluorocarbon wettability modifier of the Invention, before and after treatment.

[0016] Figure 5 shows imbibition data with a cationic surfactant wettability modifier of the Invention, before and after treatment.

[0017] Figure 6 shows brine saturation in a core before and after treatment with a fluorocarbon wettability modifier of the Invention.

Detailed Description of the Invention

[0018] A long-term solution for preventing or remediating water block and condensate banking (gas blocking) has been found. A well that does not have a water block or condensate bank problem is treated with the method to prevent formation of water blocks or condensate banks in the future. This method may also be used to clean up existing water or condensate blocks in the well and to protect against the occurrence of future water block and condensate banking. (The terms “gas banking” and “condensate banking/block” are used interchangeably here.)

[0019] Water and condensate blocks occur when a formation is liquid wet, *i.e.* either water wet or oil wet. When a well is treated using the chemical method described here, the wettability of the formation is altered from water-wet or oil-wet to intermediate or gas-wetting conditions. The alteration of wettability of a formation that is initially water or oil wet to intermediate or gas wetting creates a hydrophobic (water repelling) and oleophobic (oil repelling) surface. Because of this wettability alteration, water or condensate blocks can be cleaned up easily. The chemicals used in this method adhere to the pore walls of the formation by chemical bonding, adsorption, precipitation, aggregation, or electrostatic attraction, etc., with minimal damage, and cannot easily be

removed by the flow of liquids or gases. As a result, the induced intermediate or gas wettability by treatment with the chemical lasts for a long time, thus providing a long-term preventive solution to the formation of water and condensate blocks.

[0020] This prevention method may be applied to newly drilled oil or gas wells before putting them on production or to producing wells to prevent formation of water or condensate blocks. In cases in which the well is already affected by water or condensate blocks, use of this method enhances clean-up (flow back of water and oil that enter the formation during the operation or by cross flow) and may be used for remediation. The chemical system may be mixed with fluids used in fracturing, acidizing, drilling or other well intervention operations to unload the water or oil that may invade the formation during these operations. The wettability modifier, along with the carrier fluid, may also be pumped as a preflush or post flush before pumping a treatment such as hydraulic fracturing, acid fracturing, matrix stimulation, drilling, gravel packing, frac packing, stim packing, water packing, water fracing, lost circulation control, diversion, sand control, scale dissolution, scale removal, scale control, water control, mud damage removal, completion, mud cake cleaning, or other. The low pressure drop experienced by flowing liquids in such wettability-altered formations (altered from oil or water-wet to intermediate or gas-wet) may also be used to decrease the near wellbore pressure drop, thus enhancing both the production of oil in producing wells and the injectivity of water in injector wells. The wettability modifier adheres to the formation and creates an intermediate or gas-wetting surface that enhances the flow back of water and oil that enter the formation during the operation.

[0021] In another application of this method a producing oil well or water injection well may be treated with the carrier fluid containing a wettability modifier to alter the wettability of the formation to intermediate or gas wetting. The altered wettability increases the liquid permeability of the medium, thereby enhancing production from oil wells and injectivity of injection wells.

[0022] The invasion of water into a formation or a layer of a formation may occur when the fluid pressure, for example in a well or fracture or layer of a formation, is greater than the formation fluid pressure or the pressure in a layer, or when there is a

pressure difference between different layers in the formation, or when there is imbibition, for example from a well or fracture or another layer into a given layer or formation. For example, in hydraulic fracturing, the high injection pressure of the fluid used to fracture a well may cause water-based fracturing fluids to leak into the formation. This is very typical in a fracturing treatment and clean-up of the fluid entering the formation may or may not be a problem depending on the nature of the fluid, the nature of the formation, and the amount of fluid that enters the formation (see for example SPE paper 38620). Water may also enter the formation through imbibition, a process in which a wetting phase displaces a non-wetting phase in a porous medium. For example, if, for a porous medium, the wetting phase is water (*i.e.*, the formation is water wet) and the non-wetting phase is gas and/or oil, then if the formation contains mobile oil and/or gas, upon contact, water will imbibe into the porous medium, displacing the gas and/or oil in the medium. Once water enters the formation it may be trapped there, creating a water block if the formation fluids (oil and/or gas) cannot displace it. The reasons for water-trapping could be high capillary pressure at the water-gas or water-oil interface, interaction of water with minerals such as clays in the formation, etc. In gas wells, water trapping may also occur due to viscous fingering because the gas has lower viscosity than water. In such a case, the gas breaks through the trapped water (fingers through the water) leaving a high saturation of water near the wellbore, which creates a water block.

[0023] In condensate banking, condensate drops out of the gas phase when the gas pressure falls below the dew point pressure. This phenomenon, where liquid hydrocarbons condense out of the gas phase with a decrease in pressure below the dew point, is called retrograde condensation. Due to a steep decrease in pressure near the well bore, the well flowing pressure first falls below the dew point, at which time liquid hydrocarbons condense out of the gas phase. Due to drawdown and reservoir depletion, the pressure farther and farther away from the wellbore gradually decreases below the dew point and the condensed liquid hydrocarbon slowly accumulates, forming a condensate bank. As mentioned earlier, in addition to condensates, liquid hydrocarbons may also accumulate in the formation because of external sources.

[0024] One of the ways of enhancing clean-up of trapped water or trapped liquid hydrocarbons is by decreasing the capillary pressure at the water-gas or oil-gas interface. The capillary pressure across a gas-liquid interface is given by the Young-Laplace equation,

$$P_c = \frac{2\sigma \cos \theta}{r} \quad (\text{Eq. 1})$$

where P_c is the capillary pressure, σ is the interfacial tension at the gas-liquid interface, θ is the contact angle and r is the mean radius of curvature of the gas-liquid interface. In a porous medium, the mean radius of curvature is approximated by the mean pore size, which may be approximated further by the relation $r \sim \sqrt{k/\phi}$ where k is the permeability and ϕ is the porosity of the porous medium. Thus, in general, capillary pressure is strong in low permeability formations and weak in high permeability formations. The problem of water and condensate blocks may be reduced if the capillary pressure across the gas-liquid interface can be decreased. From Eq. 1, it can be seen that the capillary pressure can be decreased by reducing the interfacial tension between the fluid and the gas, by increasing the contact angle, or by increasing the permeability of the medium.

[0025] Addition of interfacial tension reducers such as surfactants or alcohol-based solvents can decrease the capillary pressure. However, this method is only temporary, because the conventionally used surfactants and solvents flow out of the formation once the well is put into production. If the water block or condensate-banking problem occurs again, which is to be expected because the underlying cause has not been addressed, then the well has to be re-treated with solvents or surfactants when necessary.

[0026] An alternative method of decreasing the capillary pressure is to alter the wettability of the formation or pore surface permanently in such a way that the contact angle θ of the liquid with the pore surface is increased. For example, if the contact angle is altered from 0° to 90° , then the capillary pressure can be reduced to zero (from Eq. 1), which helps in removal of water or condensate blocks. Wettability alteration for removal of water or condensate blocks is a long-term solution, because the formation wettability is permanently altered.

[0027] Wettability is defined as the ability of one fluid to spread on to a solid surface in the presence of another immiscible fluid. When two fluids, mutually immiscible with each other, both contact a solid surface, the less-wetting fluid will retreat from contact with the solid while the stronger-wetting fluid will be attracted to the surface. At the point of intersection between the two fluid phases and the solid surface, a contact angle is produced (see Figure 1). The three-phase contact angle that forms as a result of the equilibrium of the three interfacial tensions is described by Young's equation, which for a solid, liquid and gas system is shown in Eq. 2:

$$\sigma_{SG} - \sigma_{SL} = \sigma_{LG} \cos \theta$$

(Eq. 2)

where σ_{SG} is the interfacial tension between solid and gas, σ_{SL} is the interfacial tension between solid and liquid (water or oil) and σ_{LG} is the interfacial tension between the liquid (water or oil) and gas. When the contact angle is less than 50° , the surface is referred to as being water-wet or oil-wet; when it is greater than 90° , the surface is considered to be gas-wet; and the intermediate range of contact angles from 50° to 90° is considered to be representative of an intermediate wet condition. The contact angle of water with most reservoir rocks is very low, which means that these rocks are water wet. To reduce capillary pressure for removal of water blocks, the contact angle of water with the reservoir rock should be made close to or greater than 90° . Thus, the wettability of the rock has to be altered from water wet to intermediate wet or gas wetting conditions.

[0028] Experimental studies have been reported in the literature for clean-up of condensate blocks in gas condensate reservoirs by altering the wetting nature of the formation from oil or water wet to intermediate or gas wetting. Li and Firoozabadi (Li, K., and Firoozabadi, A., *SPE Reservoir Eval. & Eng.*, **3**(2), 139-149, April, 2000) have used 3M-manufactured FC722 and FC754 to alter the wettability of Berea and chalk core samples from water or oil-wet to gas-wet. FC722 is a fluoropolymer and FC754 is a cationic surfactant. They observed that FC754 could alter the wettability from strong water wetting to intermediate gas-wetting and from strong oil wetting to less oil wetting. FC722 could alter the wettability from strong water and oil wetting to

preferential gas wetting. Tang and Firoozabadi (Tang, G., and Firoozabadi, A., *SPE Reservoir Eval. & Eng.*, 427-436, December, 2002; Tang G., and Firoozabadi, A., *Transport in Porous Media*, 52, 185-211, 2003) have investigated FC722 and FC759, that are manufactured by 3M, at temperatures in the range of 25°C to 93° C. Their experiments show good wettability alteration of formations initially oil or water wet to gas wetting after treatment with FC722 and FC759.

[0029] The above laboratory studies investigated the use of wettability alteration as a remedial operation to treat gas wells affected by condensate blocks. However, experimental or field studies reported thus far have not used wettability modification as a preventive method for formation of water blocks in gas or oil wells and condensate blocks in gas wells.

[0030] The invention is a method of changing the wettability of a formation from oil wet or water wet to intermediate wet or gas wet by contacting the formation with a wettability modifier. The treatment eliminates or greatly reduces the tendency to form water blocks and condensate blocks (or condensate banking). It may be applied to prevent water blocks and/or condensate blocks in new gas wells, oil wells, oil and gas wells, and injection wells (for example in enhanced recovery), or to reduce or eliminate water blocks and/or condensate blocks in producing gas wells, oil wells, and oil and gas wells, and in injection wells. It may also be used in wells that produce other materials such as helium or carbon dioxide, or that are used for other purposes such as for material storage or disposal. It may also be used as part of a treatment (for example drilling, stimulation, or workover) of a well.

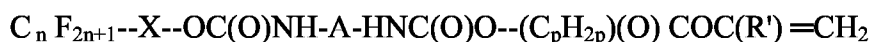
[0031] In general, the fluid used for wettability modification contains two main components, a carrier fluid, and a wettability modifier. However, the number of components may vary. The wettability modifier is dispersed or mixed or diluted in the carrier fluid to a specified concentration to achieve suitable wettability alteration from water or oil wet to intermediate or gas wetting conditions. This concentration depends upon the formation type. One method of determining a suitable concentration of a wettability modifier required for good wettability alteration is to perform a contact angle test. The concentration that gives the maximum contact angle is preferred. The carrier fluid may be, for example, water, brine, an alcohol such as methanol, isopropyl

alcohol, etc., a ketone, an ether, an ester, hydrocarbons such as petroleum distillates, diesel, biodiesel, or their derivatives, or a mixture of these solvents, but the solvent is not limited to these materials.

[0032] The wettability modifier may be a partially or completely fluorinated surfactant or polymer. One example of such a polymer is the family of fluorosilanes such as, but not limited to, 1H,1H,2H,2H-perfluorodecyltriethoxysilane, and 1H,1H,2H,2H-perfluorooctylmethyldimethoxysilane, which may be used in a concentration range of from about 0.1% to about 10% by volume, preferably at a concentration of from about 0.5% to about 2% by volume. (Note that these concentrations are expressed here as volumes of active ingredients, not as volumes of as-received commercial materials, which are usually purchased as concentrates in solvents.)

[0033] Another example of such a polymer is urethane oligomers containing perfluoro alkyl moieties, such as but not limited to those described in the following patents and published patent applications: US 20050075471, US 20040147188, US 6803109, US 6753380, US 6646088, WO 2005037884, WO 0214443, and WO 0162687. Such materials may also be used in a concentration range of from about 0.1% to about 10% by volume, preferably at a concentration of from about 0.5% to about 2% by volume (based on active ingredients).

[0034] Yet another example of such a polymer is fluoroacrylates that have the general formula:



in which n is 1 to 5; X is $-SO_2-M(R)-C_m H_{2m}-$, $-CO-NH-C_m H_{2m}-$,

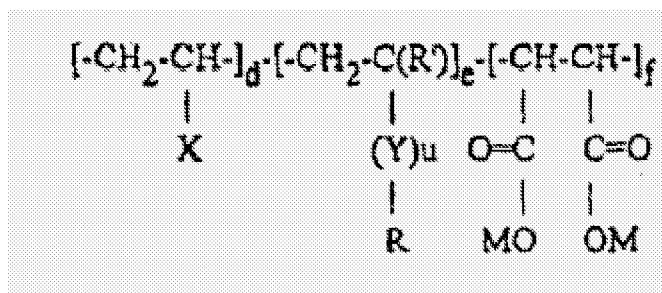
$-CH(R_f)-C_y H_{2y}-$, or $-C_q H_{2q}-$; R is H or an alkyl group of from 1 to 4 carbon atoms;

m is 2 to 8; R_f is $C_n F_{2n+1}$; y is 0 to 6; q is 1 to 8; A is an unbranched symmetric alkylene group, arylene group, or aralkylene group; p is 2 to 30; and R' is H, CH_3 , or F.

Examples of this are given in patent applications US20050143541 and

WO2005066224. Such materials may also be used in a concentration range of from about 0.1% to about 10% by volume, preferably at a concentration of from about 0.5% to about 2% by volume (based on active ingredients).

[0035] Another example of such a polymer is a fluoroalkyl containing terpolymer of the type described in US5945493, US6238792, and US6245116:



wherein X is a C 2-10 alkyl, C 6-12 aryl, or C 4-12 alkoxy radical, d is from about 3 to about 50, R is a fluoroalkyl radical $\text{R}_f \text{--}(\text{A})_v \text{--}(\text{B})_w \text{--}$, R_f is a fully fluorinated straight or branched aliphatic radical optionally interrupted by at least one oxygen atom, A is a divalent radical selected from $\text{--SO}_2 \text{N}(\text{R}'')\text{--}$, $\text{--CON}(\text{R}'')\text{--}$, --S-- , or $\text{--SO}_2\text{--}$, where R'' is H, or a C 1-6 alkyl radical, B is a divalent linear hydrocarbon radical $\text{--C}_t\text{H}_{2t}\text{--}$, where t is 1 to 12, Y is a divalent radical $\text{--CH}_2\text{--O--}$, u, v, and w are each independently zero or 1, R' is hydrogen or methyl, e is from about 0.05 to about 10, M is hydrogen, alkali metal, or ammonium, and f is from about 5 to about 40. Such materials may also be used in a concentration range of from about 0.1% to about 10% by volume, preferably at a concentration of from about 0.5% to about 2% by volume (based on active ingredients).

[0036] Examples of suitable surfactants are those used as viscoelastic surfactants in fracturing fluids. Suitable cationic surfactants of this type, such as quaternary amines, such as erucyl bis-(2-hydroxyethyl) methyl ammonium chloride, are described in US Patent Nos. 5,964,295, 5,979,557, 6,306,800 and 6,435,277; suitable zwitterionic surfactants of this type, such as betaines, such as erucic amidopropyl dimethyl betaine are described in US Patent Nos. 6,258,859 and 6,399,546. Suitable cationic surfactants that may be used include those that are commonly used as emulsifiers, such as cocoalkyl amines, cocoalkyl acetates, cocoalkyl betaines, tallow alkyl amine acetates, cocoamphodiacetates, cocoamidobetaines, and their mixtures with or without cosurfactants, solvents, paraffins, and hydrocarbons. Suitable anionic surfactants may be based on phosphate head groups (for example branched alcohol ethoxylate phosphate esters). These surfactants are not adsorbed as strongly as are the

fluoropolymers, so they work best at lower temperatures, and the effects may not be as long-lasting, especially at higher temperatures. These surfactants may also be used in the concentration range of from about 0.1% to about 10% by volume, preferably at a concentration of from about 0.5% to about 2% by volume (based on active ingredients).

[0037] The compositions and methods may be used as stand-alone treatments intended to prevent or remediate water blocks and gas or condensate banking, or the wettability modifiers can be used in other treatment fluids. Thus, in addition to stand-alone treatments, the compositions of the Invention may be added to a number of main treatment fluids with beneficial results. Examples are drilling fluids, completion fluids, stimulation fluids, for example matrix treatment fluids, fracture fluids and gravel packing fluids. When used in drilling and completion fluids, the compositions prevent the formation of water blocks. When used as additives in stimulation fluids in production wells, the compositions speed up and increase the extent of clean up and increase oil and gas production after the treatment. When used as additives in stimulation fluids in water injection wells, the compositions of the Invention increase injectivity. Alternatively, treatments may be done as a pre-treatment before stimulation, or as a post treatment after drilling, completion, and stimulation. In another use, fluids containing the wettability modifiers may be selectively introduced into certain layers of a multilayer formation (for example by isolating them with packers), to alter the wettability of those layers, and thereby alter either the relative productivity or injectivity of those layers, or the relative permeability to oil/gas or water of those layers.

[0038] Other treatment fluids are known for use in stand-alone treatments; these are generally mixtures of components such as alcohols, mutual solvents, ethers, esters, ketones hydrocarbons, and mixtures of these. These fluids may alter the wettability, but the effect is usually temporary. The compositions of the Invention may be added to such fluids, especially at low temperatures, to make the effects more long-lasting so that the single fluid treatment can act as both a remedial and a prevention treatment.

Examples:

[0039] Two types of tests were conducted to check the ability of chemical systems to alter wettability. First a contact angle test was performed, followed by an imbibition test.

[0040] Wettability in a water-gas-rock system was determined by observing the contact angle made by a drop of water [2] on a rock [4] with gas [6] as the third phase (see Figure 1). The angle θ was measured from the rock-water interface through the liquid to the water-gas interface as shown in Figure 1. When the angle θ was small, then water was said to wet the rock or the rock was water-wet in nature. When the angle θ was large, then water did not wet the rock or the rock was intermediate gas wetting. The observation was similarly extended to oil-gas-rock systems.

[0041] In a porous medium, the ability of water to wet the medium was determined by means of an imbibition test. Imbibition is the process in which a wetting phase displaces a non-wetting phase in a porous medium. The experimental apparatus used for the tests is shown in Figure 2. In this test, a dry core [8] of known porosity and permeability was brought into contact with a liquid [10], for example water, such that one end of the core was slightly immersed in the liquid. Because of capillary pressure the liquid rose into the core, displacing the air inside the core. The amount of liquid that had imbibed into the core was estimated by measuring the decrease in mass of liquid with the scale [12]. The core was suspended from a line [14] connected to a stand [16]. In general, if the core was initially water wet then the amount of water imbibed was more than 40% of the void volume inside the core. However, this percentage changed depending upon the capillary pressure, which in turn depended upon the water-gas interfacial tension, and upon core properties such as permeability, porosity, etc. (see Eq. 1). Similarly, the oil wetting nature of the core was estimated using oil instead of water as the liquid phase for the imbibition test.

[0042] Typically, a pair of imbibition tests was performed. First, an imbibition test was performed on a dry core to establish the initial wettability of the core. Then the core was treated with a solution containing the wettability modifier and a solvent that was either alcohol-based or water-based, by flowing the solution through the core and soaking the core in the solution for a period of time that depended on the wettability modifier used and on the temperature. Tests were also conducted to determine the

errors due to evaporation, and corrections were made. The wettability modifier is believed to adhere to the surface of the pores inside the core in this test. Then the core was dried and an imbibition test was again performed to check the liquid imbibition rate and volume. If either the rate of liquid intake or total volume of liquid imbibed decreased when compared to the initial imbibition test before treatment with the wettability modifying solution then the wettability was considered to have been altered to an intermediate or gas wetting nature.

[0043] To judge the ability of the method and of a specific wettability modifier to alter wettability of the formation so that prevention of water blocks was achieved, the following tests were conducted. Cores used were typical sandstones, such as Berea, from Ohio, U. S. A., Bandera, from Kansas, U. S. A., and Tunu from Indonesia; the latter contains carbonates. The choice of sandstone made little difference in the tests with these three sandstones, and similar results are expected with carbonate cores. First, the contact angle of water with a dry core chip (a thin slice of a core) was observed by placing a drop of water on the core. Then the core chip was treated with a solution containing a wettability modifier by soaking it in the solution. Then the core chip was dried and a drop of water was placed on it to check the contact angle. If the contact angle was more than the initial contact angle, then the wettability modifier had increased the gas wetting nature of the core, which was desired for prevention of water blocks.

[0044] A soak (shut in period) may optionally be used in the method of the invention. Whether or not a soak is required in practice depends upon the formation, and its temperature, and the choice of the wettability modifier. Not to be limited by theory, but it is believed that if a head group of the wettability modifier, for example a silane head group, reacts with the surface of the formation, for example in the pores, for example quartz components, this occurs more rapidly at higher temperature, so less soak time or no time will be required at higher temperatures for such materials.

[0045] Formation minerals affect the adsorption of surfactants, depending upon the head group charge and the charge of the mineral surface, and this affects the required shut-in period. Consequently, at higher temperatures desorption may occur and wettability modifiers that act by adsorption may perform better at low temperature than

at high temperature. These factors may be tested by simple laboratory experiments with core samples and wettability modifier chemicals.

Example 1:

[0046] The contact angle test on a core chip was observed using water as the fluid phase, before and after treatment with a wettability modifier (Rhodafac-PA-32[®], a linear alcohol ethoxylate phosphate ester, available from Rhodia Inc., Cranbury, New Jersey, U. S. A.). Before treatment, water spread on the core chip (the contact angle was close to zero) showing that the core was water-wet. After treatment the contact angle was greater than 90° showing that the wettability had been altered to gas wetting.

Example 2:

[0047] Figure 3 shows the data from an initial imbibition test on a dry core and then an imbibition test on the same core after treatment with Zonyl 8740[®]. Zonyl 8740[®] is an aqueous dispersion containing 30% by weight of a perfluoroalkyl methacrylic copolymer. It is commercially available from DuPont Specialty Chemicals, Wilmington, DE, U. S. A., and is described as being a “waterborne oil and water repellent” material. The y-axis shows the percentage of void volume in the core occupied by water as a function of time. Before treatment, 55% of the void volume was filled with water in less than 50 minutes, showing that the core was water-wet. After treatment with the wettability modifier, the water intake was drastically reduced, showing that the wettability of the core had been changed from water-wet to gas wetting.

Example 3:

[0048] The contact angle test was performed on a core chip that had been treated with a solution of 5% Zonyl 8740[®] + 93 % water + 2% KCl. The contact angle was greater than 90° after the treatment, indicating that the wettability had been altered to gas wetting. The imbibition test data for this fluid system was given in example 2. From the contact angle and imbibition data it can be seen that this system may be used for prevention of water blocks. The contact angle test was also performed on a core chip

that had been treated with a dilute solution of Novec[®] fluorosurfactant FC-4430, available from 3M, Performance Materials Division, St. Paul, MN, U. S. A. This material is a non-ionic polymeric fluorochemical surfactant (fluoroaliphatic polymeric esters) obtained as a solution that was 2%, in water and methanol, of a mixture that had been 90% active ingredient, 8% non-fluorochemical additives (polyether polymer), and 2% N-methyl-2-pyrrolidone/toluene solvent. From the contact angle data (not shown) it was seen that this system may be used for prevention of water blocks. Similar experiments were also done to evaluate the performance of additives to prevent condensate banking.

Example 4:

[0049] Figure 4 shows the results of imbibition tests made with the wettability modifier SRC-220[®], a commercial fluorochemical urethane material obtained from 3M Specialty Materials, St. Paul, MN, U. S. A, and described as a “Stain Resistant Additive”. As received, the material is 19-22% active material, 70-76% water, and 4-7% 2-methoxymethylethoxypropanol. It was used as 2% SRC-220[®] + 96% of 50% isopropyl alcohol + 2% KCl. The contact angle test showed that the wettability of the rock was changed to gas wetting conditions (the contact angle was greater than 90° after the treatment). Figure 4 shows that the initial imbibition into the core was 45 % of the void volume of the core. After treatment with the fluid, the final imbibition volume was reduced to 10%, which shows that the system may be used for water block and condensate banking prevention.

Example 5:

[0050] Figure 5 shows the results of imbibition tests with a wettability modifier that is a cationic surfactant; it was obtained from Baker Petrolite, Sugar Land, TX, U. S. A., as Aquet 942[®], which is supplied as about 50% active ingredient and about 50% organic solvents. It was used as 5% Aquet 942[®] + 93 % of 50% isopropyl alcohol + 2% KCl. The contact angle test showed that the wettability was altered to gas wetting conditions (the contact angle was greater than 90° after the treatment). The imbibition data showed that, before treatment with the chemical system, over 90% water was imbibed

in a little over 150 minutes, and that after treatment with the chemical the imbibition rate of water and the total water imbibed were drastically reduced.

Example 6:

[0051] Several tests were performed using cationic, anionic, and zwitterionic surfactants, fluorosurfactants, and fluoropolymer based chemicals to check their ability to alter wettability of the formation and thereby to prevent water block formation. Table 1 shows the experimental data. T1 was the time taken for 60% imbibition of water before treatment with the chemical, and T2 was the time taken for 60% imbibition of water after treatment with the chemical. The ratio of T2/T1 is a convenient measure of the ability of the chemical to alter the wettability of the formation. A large ratio indicates better wettability alteration; “inf” means infinite.

Chemical	(Vol%)	T1 (min)	T2 (min)	T2/T1
Aquet 942 [®]	5	63	786	12.5
Cationic Surfactant A	5	63	612	9.7
Cationic Surfactant B	5	83	1210	14.6
Cationic Surfactant C	5	42	954	22.7
Cationic Surfactant D	5	20	84	4.2
Zwitterionic Surfactant	2	10	38	3.8
3M SRC-220 [®] (Fluoropolymer)	2	16	inf	inf
Dupont Zonyl 8470 [®] (Fluorosurfactant)	5	40	inf	inf
Rhodia Rhodafac PA-32 [®]	5	16	117	7.3

Table 1

Cationic Surfactants A and B are blends of cocoalkyl amines and acetates. Cationic Surfactant C is N-cis-13-docosenoic-N,N,-bis(2-hydroxymethyl)-N-methyl ammonium chloride. Cationic Surfactant D is a mixture of alkyl and alkenyl bis(2-hydroxyethyl) ammonium chlorides. Zwitterionic Surfactant is erucic amidopropyl dimethyl betaine. Note that the concentrations given in Table 1 are of as-received material concentrates including solvents.

Example 8: Core Test

[0052] A different type of test was performed to determine the effectiveness, the extent of possible damage imparted by this chemical, and the permanency of the treatments of the Invention. A core test was conducted at 126.6 °C (260 °F) using a standard Hassler cell. In this test, the core (length = 6.35 cm; diameter = 3.77 cm, permeability = 12 mD, porosity = 14%) was initially saturated with 6% KCl brine, and N₂ gas was then injected into the core to displace water. The removal of water was measured by applying different gas pressure gradients along the length of the core and weighing the water expelled from the core at each pressure gradient. Then the core was treated with a solution containing 5% Zonyl 8470[®] and 95% of 6% KCl brine, by injecting 5 pore volumes of the solution into the core; the core was not shut-in. After the treatment, 6% KCl brine was injected into the core as a post flush to displace the treatment solution. Once the core was fully saturated with brine, N₂ gas was again injected at three different pressure gradients, and the water removed from the core was measured and compared to that obtained before treatment. After this stage, four more brine-gas cycles were done (to check the long-term efficiency of the system); in these, the core was again saturated with brine and then a gas flush was performed to measure the water expelled from the core. Note that from the brine that was expelled from the core, the remaining brine saturation could be calculated since the porosity of the core was known.

[0053] Figure 6 (the data are shown in Table 2) shows the brine saturations (S_w) in the untreated and treated core when the three different gas pressure gradients were applied across the core. For the untreated core, the brine saturations in the core were 73%, 58% and 57%, at differential pressures of 0.034 MPa (5 psi), 0.103 MPa (15 psi) and 0.276 MPa (40 psi) respectively. When the pressure gradient was increased from 0.103 MPa (15 psi) to 0.276 MPa (40 psi), the additional water removed was very low for the untreated core. The additional decrease in brine saturation was only 1%. This shows that a large amount of brine was trapped in small pores whose capillary entry pressure was greater than 0.276 MPa (40 psi).

[0054] After treatment (cycles 1-5), the brine saturation in the core was lower than that of the untreated core at all pressure gradients. This was due to capillary pressure reduction by Zonyl 8470[®] which allowed the clean up of water from smaller pores.

When differential pressure was increased from 0.103 MPa (15 psi) to 0.276 MPa (40 psi), reduction in brine saturation was in the range of 6% - 13%, compared to 1% before treatment. The slope of the lines between 0.103 MPa (15 psi) and 0.276 MPa (40 psi), after treatment showed that higher differential pressures resulted in further clean up. Before treatment, the line was almost vertical, showing that increasing pressure did not enhance clean up at the same rate as for a treated core.

	$\Delta P1$ (MPa)	Sw1	$\Delta P2$ (MPa)	Sw2	$\Delta P3$ (MPa)	Sw3
Untreated	0.032	0.73	0.106	0.58	0.278	0.57
Treated						
Cycle 1	0.037	0.65	0.099	0.55	0.273	0.45
Cycle 2	0.057	0.65	0.110	0.56	0.272	0.49
Cycle 3	0.055	0.67	0.113	0.58	0.272	0.45
Cycle 4	0.038	0.58	0.103	0.49	0.276	0.42
Cycle 5	0.035	0.67	0.101	0.54	0.273	0.48

Table 2

Example 9: Field Application

[0055] A typical field application of this method may have three stages: pretreatment, main treatment, and post treatment stages. In the pretreatment stage, a preflush fluid is injected into the formation. The fluid may contain brine, solvent, organic or inorganic clay stabilizer solution, matrix stimulation fluids, etc. In the main stage, a carrier fluid containing the wettability modifier, solvents and other components, is pumped into the formation. The fluid is then left in the formation for a period of time that depends upon the fluid and upon the temperature of the formation. In some cases, it may not be necessary to leave the fluid in the formation. The wettability modifier adheres to the pore walls in the formation either by adsorption, by chemical bonding, by precipitation, by aggregation or by electrostatic attraction. Following the main stage, a post treatment stage may optionally be performed, either immediately after the main stage or after the shut-in period. In the post treatment stage, a gas, foam or brine may be injected into the formation to displace the main stage fluid further into the formation or to spread the wettability modifier uniformly. The post treatment stage may also be done to enhance the flow back of the carrier fluid, solvents, and excess wettability

modifier injected in the main stage. When the well is put on production, the fluids flow back to the surface, leaving a coating of wettability modifier on the pore walls of the formation. Because of the wettability modifier, the formation becomes intermediate or gas wetting, which prevents the formation of water or condensate blocks. The treatment will be long-lasting.

Claims

1. In a subterranean formation penetrated by a well bore, the formation containing an accumulation of liquid, selected from water, oil, condensate, and mixtures thereof, that is blocking at least some flow of fluid in the formation, a method for removing at least a portion of the accumulation of liquid, selected from water, oil, condensate, and mixtures thereof, by altering the wettability of the formation from an initially oil or water wet state to an intermediate or gas wet state, comprising the step of contacting the formation with a treatment fluid comprising a wettability modifier.
2. In a subterranean formation penetrated by a well bore, a method for reducing the formation of an accumulation of liquid, selected from water, oil, condensate, and mixtures thereof, that would block the flow of fluid, by altering the wettability of the formation from an initially oil or water wet state to an intermediate or gas wetting state by the step of contacting the formation with a wettability modifier.
3. In a subterranean formation penetrated by a well bore, a method for preventing the formation of an accumulation of liquid, selected from water, oil, condensate, and mixtures thereof, that would block the flow of fluid, by altering the wettability of the formation from an initially oil or water wet state to an intermediate or gas wetting state by the step of contacting the formation with a wettability modifier.
4. The method of any of the preceding claims wherein the step of contacting is preceded by a preflush step.
5. The method of any of the preceding claims wherein the step of contacting is followed by a postflush step.
6. The method of any of the preceding claims wherein the step of contacting further comprises a soak period.
7. The method of any of the preceding claims wherein the treatment fluid comprises more than one wettability modifier.
8. The method of any of the preceding claims wherein the wettability modifier is selected from the group consisting of cationic surfactants, quaternary

amines, erucyl bis-(2-hydroxyethyl) methyl ammonium chloride, zwitterionic surfactants, betaines, erucic amidopropyl dimethyl betaine, cocoalkyl betaines, cocoamido betaines, cocoalkyl amines, cocoalkyl acetates, tallow alkyl amine acetates, and cocoamphodiacetates.

9. The method of any of the preceding claims wherein the wettability modifier is selected from the group consisting of fluorosurfactants and fluoropolymers.
10. The method of claim 9 wherein the fluoropolymers are selected from the group consisting of fluorosilanes, fluoroalkoxysilanes, polymeric fluoroacrylates, perfluoro alkyl urethane oligomers, and mixtures thereof.
11. The method of any of the preceding claims wherein the wettability modifier is present in a concentration of between about 0.1 per cent by volume and about 10 per cent by volume, preferably between about 0.5 per cent by volume and about 5 per cent by volume based on active material.
12. The method of any of the preceding claims wherein the step of contacting the formation with a wettability modifier comprises incorporating the wettability modifier in a treatment fluid selected from the group consisting of drilling fluids, completion fluids, and stimulation fluids.

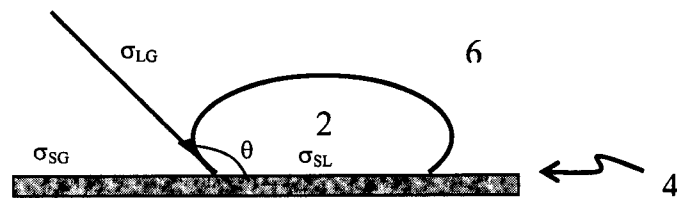


Fig.1

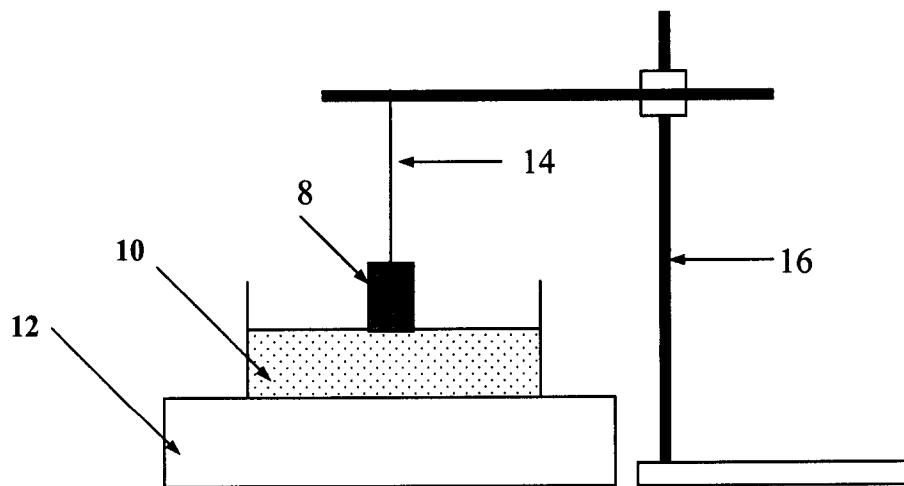


Fig. 2

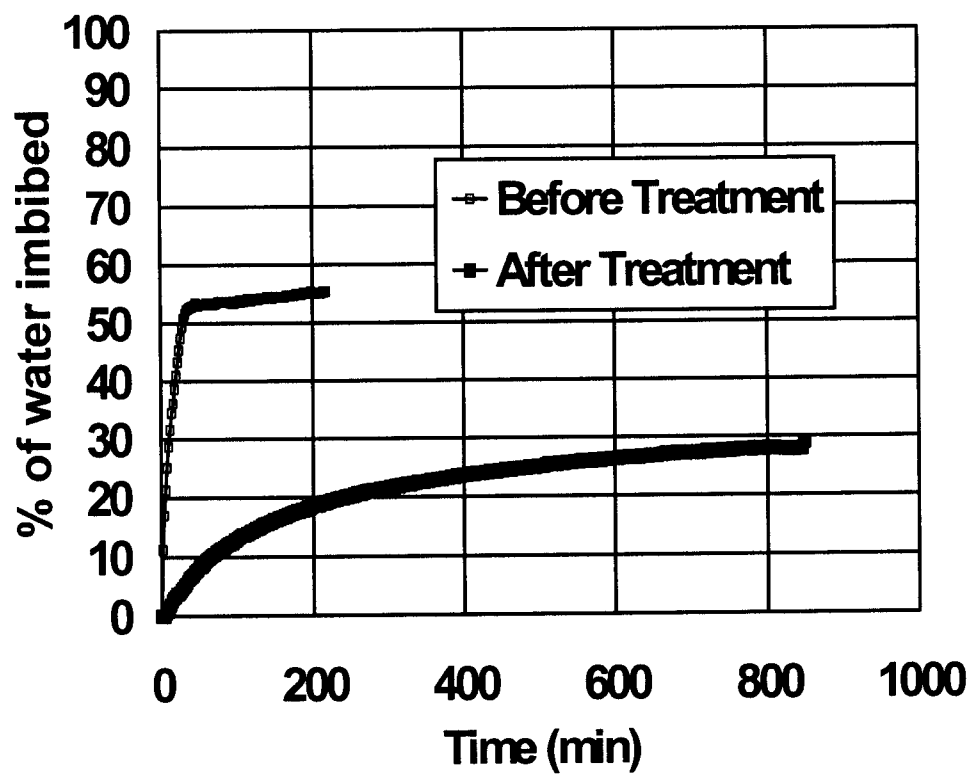
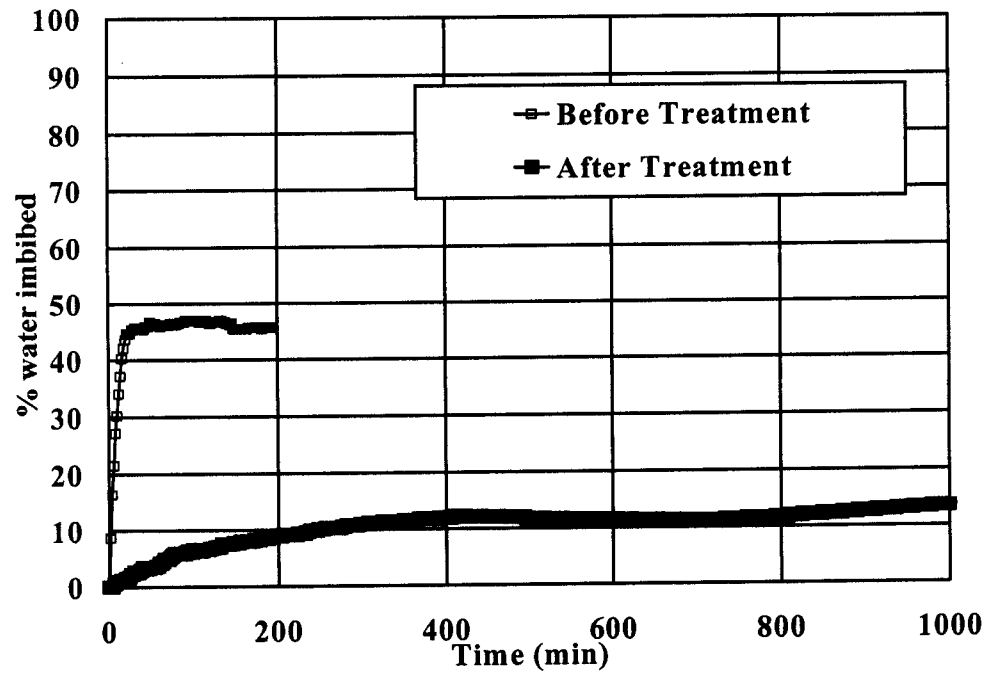
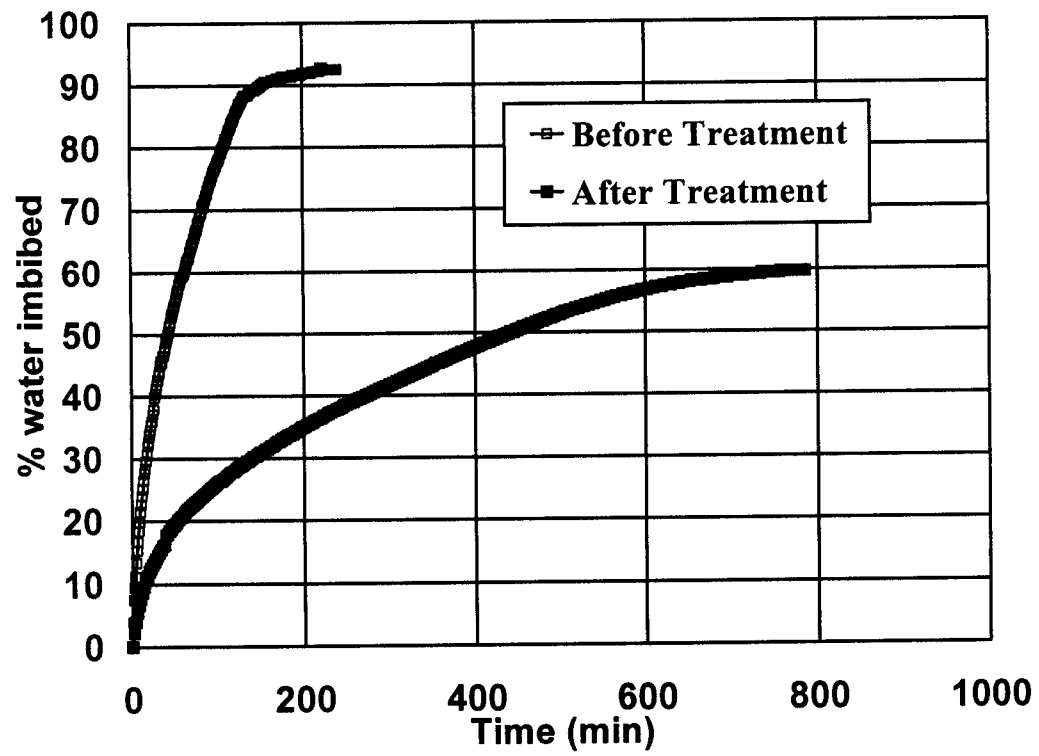


Fig. 3

**Fig. 4**

**Fig. 5**

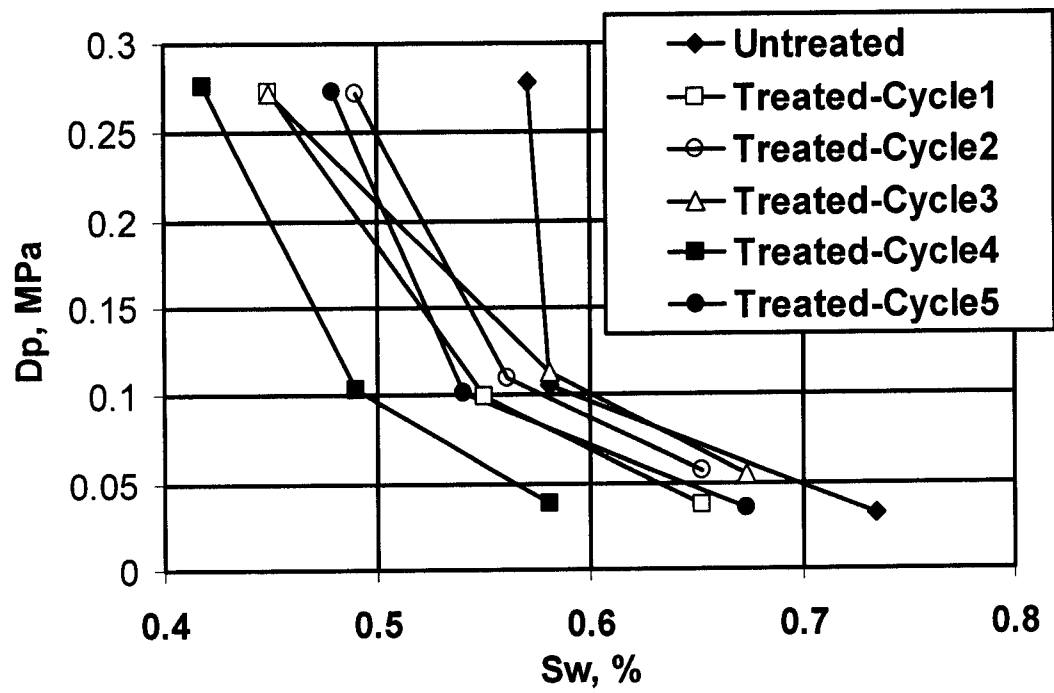


Fig. 6