Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2675126 C 2011/12/06

(11)(21) **2 675 126**

(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

(86) **Date de dépôt PCT/PCT Filing Date**: 2008/01/17

(87) **Date publication PCT/PCT Publication Date**: 2008/07/24

(45) **Date de délivrance/Issue Date**: 2011/12/06

(85) **Entrée phase nationale/National Entry**: 2009/07/09

(86) **N° demande PCT/PCT Application No.**: GB 2008/000190

(87) **N° publication PCT/PCT Publication No.**: 2008/087444

(30) **Priorités/Priorities**: 2007/01/19 (US11/655,403);
2007/01/19 (US11/655,402)

(51) **Cl.Int./Int.Cl.** *C09K 8/64* (2006.01),
C09K 8/68 (2006.01), *C09K 8/82* (2006.01),
C09K 8/88 (2006.01), *E21B 43/25* (2006.01)

(72) **Inventeurs/Inventors**:
REDDY, B. RAGHAVA, US;
EOFF, LARRY STEVEN, US;
ZHANG, DANHUA LESLIE, US;
DALRYMPLE, ELDON DWYANN, US;
BROWN, PAUL S., US

(73) **Propriétaire/Owner**:
HALLIBURTON ENERGY SERVICES, INC., US

(74) **Agent**: NORTON ROSE OR S.E.N.C.R.L., S.R.L./LLP

(54) **Titre** : COMPOSITIONS DESTINEES A AUGMENTER LA PRODUCTION DE GAZ D'UNE FORMATION SOUTERRAINE

(54) **Title**: COMPOSITIONS FOR INCREASING GAS PRODUCTION FROM A SUBTERRANEAN FORMATION

(57) **Abrégé/Abstract**:

The invention relates to treatment fluids for treating a subterranean formation to improve gas production therefrom. Exemplary embodiments of the treatment fluids comprise a base fluid and a cationic polyorganosiloxane, wherein the cationic polyorganosiloxane comprises at least two cationic quaternary ammonium groups. The invention also relates to methods of treating a subterranean formation to improve gas production therefrom.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 July 2008 (24.07.2008)

PCT

(10) International Publication Number
WO 2008/087444 A1

(51) International Patent Classification:
C09K 8/64 (2006.01) *C09K 8/82* (2006.01)
C09K 8/68 (2006.01) *C09K 8/88* (2006.01)

(21) International Application Number: PCT/GB2008/000190

(22) International Filing Date: 17 January 2008 (17.01.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/655,402 19 January 2007 (19.01.2007) US
11/655,403 19 January 2007 (19.01.2007) US

(71) Applicant *(for all designated States except US)*: **HALLIBURTON ENERGY SERVICES, INC.** [US/US]; P.O. Box 1431, Duncan, OK 73533 (US).

(71) Applicant *(for MW only)*: **CURTIS, Philip, Anthony** [GB/GB]; A A Thornton & Co, 235 High Holborn, London WC1V 7LE (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **REDDY, B., Raghava** [IN/US]; 2013 Waverly Drive, Duncan, OK 73533 (US). **EOFF, Larry, Steven** [US/US]; 2201 Cedar Avenue, Duncan, OK 73533 (US). **ZHANG, Danhua, Leslie** [CN/US]; 1710 W. Plato Road, Apt #806, Duncan, OK 73533 (US). **DALRYMPLE, Eldon, Dwyann** [US/US]; 907 East Plato Road, Duncan, OK 73533 (US). **BROWN, Paul, S.** [US/US]; 2217 Spruce, Duncan, OK 73533 (US).

(74) Agents: CURTIS, Philip, Anthony et al.; A A Thornton & Co, 235 High Holborn, London WC1V 7LE (GB).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

WO 2008/087444 A1

(54) Title: COMPOSITIONS FOR INCREASING GAS PRODUCTION FROM A SUBTERRANEAN FORMATION

(57) Abstract: The invention relates to treatment fluids for treating a subterranean formation to improve gas production therefrom. Exemplary embodiments of the treatment fluids comprise a base fluid and a cationic polyorganosiloxane, wherein the cationic polyorganosiloxane comprises at least two cationic quaternary ammonium groups. The invention also relates to methods of treating a subterranean formation to improve gas production therefrom.

COMPOSITIONS FOR INCREASING GAS PRODUCTION FROM A SUBTERRANEAN FORMATION

BACKGROUND

[0001] The present invention relates to compositions for increasing gas production from a subterranean formation. More particularly, the present invention relates to treatment fluids for treating a subterranean formation to improve the production of gas therefrom, the treatment fluids comprising a cationic polyorganosiloxane comprising at least two quaternary ammonium groups.

[0002] The present invention also relates to methods for increasing gas production from a subterranean formation. More particularly, the present invention relates to the treatment of a subterranean formation with a cationic polyorganosiloxane comprising at least two quaternary ammonium groups to reduce water blocks in the treated portion of the formation.

[0003] Hydrocarbon gases (*e.g.*, natural gas) are found in subterranean formations beneath the Earth's surface. To obtain these gases, well bores are drilled into the gas-bearing formations through which the gas is produced to the surface. Gas production rates from these formations, however, are often less than expected or desired due to a variety of factors. One common factor for lower gas production rates is the presence of water in the flow channels available for gas flow. This water reduces the effective permeability of the formation to the natural gas and is commonly referred to as "water blocks."

[0004] The source of water contributing to the water blocks generally depends on the location of the water blocks themselves. For example, near well bore water blocks may be due to the invasion of water present in the well bore from well operations or from produced water. This water from the well bore may be imbibed by near well bore permeable zones into the flow channels and, thus, reduce gas production. If the water blocks are present in flow channels away from the well bore, the source of water may be due to the connate water held in permeable formation zones due to high capillary pressure. As this connate water moves toward the well bore with continued gas production, it may become trapped in some permeable zones, such as low permeability zones, thus blocking the flow of the gas. The source of water may also be from reservoir stimulation operations (*e.g.*, matrix acidizing, fracturing, water control treatments with relative permeability modifiers, and the like), in which the injected fluids penetrate into the formation. However, in all these examples, if the natural drainage rates (*e.g.*, due to gravity) or induced drainage rates (*e.g.*, due to gas pressure) for the water are low, the water blocks will typically remain in the gas flow channels. As a result, the water blocks will reduce, or in some instances completely shut off, the production of gas from the formation. In some instances, water blocks may even delay gas production for a significant period of time after stimulation treatments.

SUMMARY

[0005] The present invention relates to compositions for increasing natural gas production from a subterranean formation. More particularly, the present invention relates to treatment fluids for treating a subterranean formation to improve the production of gas therefrom, the treatment fluids comprising a cationic polyorganosiloxane comprising at least two quaternary ammonium groups.

[0006] The present invention also relates to methods for increasing natural gas production from a subterranean formation. More particularly, the present invention relates to the treatment of a subterranean formation with a cationic polyorganosiloxane comprising at least two quaternary ammonium groups to reduce water blocks in the treated portion of the formation.

[0007] In one aspect, the present invention provides a treatment fluid for treating a subterranean formation to improve gas production therefrom. The treatment fluid comprises a base fluid and a cationic polyorganosiloxane, wherein the cationic polyorganosiloxane comprises at least two cationic quaternary ammonium groups. In one exemplary embodiment, the base fluid comprises an aqueous fluid and the cationic polyorganosiloxane is water-soluble. In another exemplary embodiment, the base fluid comprises a non-aqueous fluid and the cationic polyorganosiloxane is non-aqueous fluid soluble.

[0008] In another aspect, the present invention provides a method of treating a subterranean formation to improve gas production therefrom. The method comprises introducing a cationic polyorganosiloxane into the subterranean formation, wherein the cationic polyorganosiloxane comprises at least two quaternary ammonium groups.

[0009] In another aspect, the present invention provides a method of treating a subterranean formation to improve gas production therefrom. The method comprises introducing a treatment fluid into a well bore that penetrates the subterranean formation so as to contact the subterranean formation with the treatment fluid. The treatment fluid comprises a base fluid and a cationic polydimethylsiloxane, wherein the cationic polydimethylsiloxane comprises at least two quaternary ammonium groups. Treatment of the subterranean formation with the cationic polydimethylsiloxane improves gas production from the subterranean formation.

[0010] In another aspect, the present invention provides a method of treating a coalbed to improve gas production therefrom. The method comprises introducing a treatment fluid into a well bore that penetrates the coalbed so as to contact the coalbed with the treatment fluid. The treatment fluid comprises methanol and a cationic polydimethylsiloxane, wherein the cationic polydimethylsiloxane comprises at least two quaternary ammonium groups.

[0011] The features and advantages of the present invention will be apparent to those skilled in the art upon reading the following description of specific embodiments with reference to the accompanying drawings.

DRAWINGS

[0012] FIG. 1 is a graph of percent brine imbibition for Berea sandstone cores treated with certain materials in a kerosene-based carrier fluid;

[0013] FIG. 2 is a graph of percent residual water saturation for Berea sandstone cores treated with certain materials in a brine-based carrier fluid;

[0014] FIG. 3 is a graph of brine imbibition and percent residual water saturation for Berea sandstone cores treated with certain materials in a brine-based carrier fluid;

[0015] FIG. 4 is a graph of residual water saturation as a function of time for Berea sandstone cores treated with certain materials in a brine-based carrier fluid;

[0016] FIG. 5 is a graph of percent brine imbibition for Berea sandstone cores treated with certain materials in a methanol-based carrier fluid;

[0017] FIG. 6 is a graph of percent brine imbibition for Berea sandstone cores treated with certain materials in a methanol-based carrier fluid; and

[0018] FIG. 7 is a graph of residual water saturation as a function of time for Berea sandstone cores treated with certain materials in a methanol-based carrier fluid.

DESCRIPTION OF SPECIFIC EMBODIMENTS

[0019] The present invention relates to compositions for increasing natural gas production from a subterranean formation. More particularly, the present invention relates to treatment fluids for treating a subterranean formation to improve the production of gas therefrom, the treatment fluids comprising a cationic polyorganosiloxane comprising at least two quaternary ammonium groups.

[0020] The present invention also relates to methods for increasing natural gas production from a subterranean formation. More particularly, the present invention relates to the treatment of a subterranean formation with a cationic polyorganosiloxane comprising at least two quaternary ammonium groups to reduce water blocks in the treated portion of the formation.

[0021] As used herein, the term "polyorganosiloxane" is used to refer to a polymer containing a polymer backbone of Si-O-Si bonds, wherein the silicon atoms in the polymer backbone are connected to alkyl groups via Si-C bonds except at the chain ends and branching points where the silicon atoms may be connected to either carbon or other atoms such as oxygen, nitrogen or sulfur and the like.

[0022] As will be appreciated by those of ordinary skill in the art, exemplary embodiments of the compositions and methods of the present invention may be used in any subterranean formation containing gas. This gas may be compressed gas contained within formation pores and/or gas that is adsorbed onto surfaces within the formation. By way of example, the techniques described herein may be used to treat coal beds to improve the recovery of natural gas found therein. Those of ordinary skill in the art will appreciate that gas found in coal beds is commonly referred to as "coalbed methane."

[0023] In accordance with exemplary embodiments of the present invention, a treatment fluid for treating a subterranean formation to improve the production of gas generally comprises a carrier fluid and a cationic polyorganosiloxane comprising at least two quaternary ammonium groups. The cationic polyorganosiloxane should improve gas production by reducing the occurrence of water blocks in the treated portion of the formation. Without being limited by theory, once introduced into the formation, the cationic polyorganosiloxane should adsorb onto surfaces in the treated portion of the formation. Once adsorbed, it is believed that the cationic polyoganosiloxane may increase the contact angle between water and formation surfaces. This may directly or indirectly lead to reduced capillary pressure in the porosity of the formation. Reduced capillary pressure may lead to increased water-drainage rates. As will be appreciated, improved water-drainage rates should allow a reduction in existing water blocks, as well as a reduction in the formation of water blocks. Moreover, it is also believed that the cationic polyorganosiloxane may reduce the tendency of the formation to imbibe water in the gas flow channels. In other words, it is believed that the cationic polyorganosiloxane should reduce the water-imbibition rates of the treated portion of the formation. As such, it is believed that treatment of the formation with the polyorganosiloxane may reduce the formation of water blocks in the treatment portion.

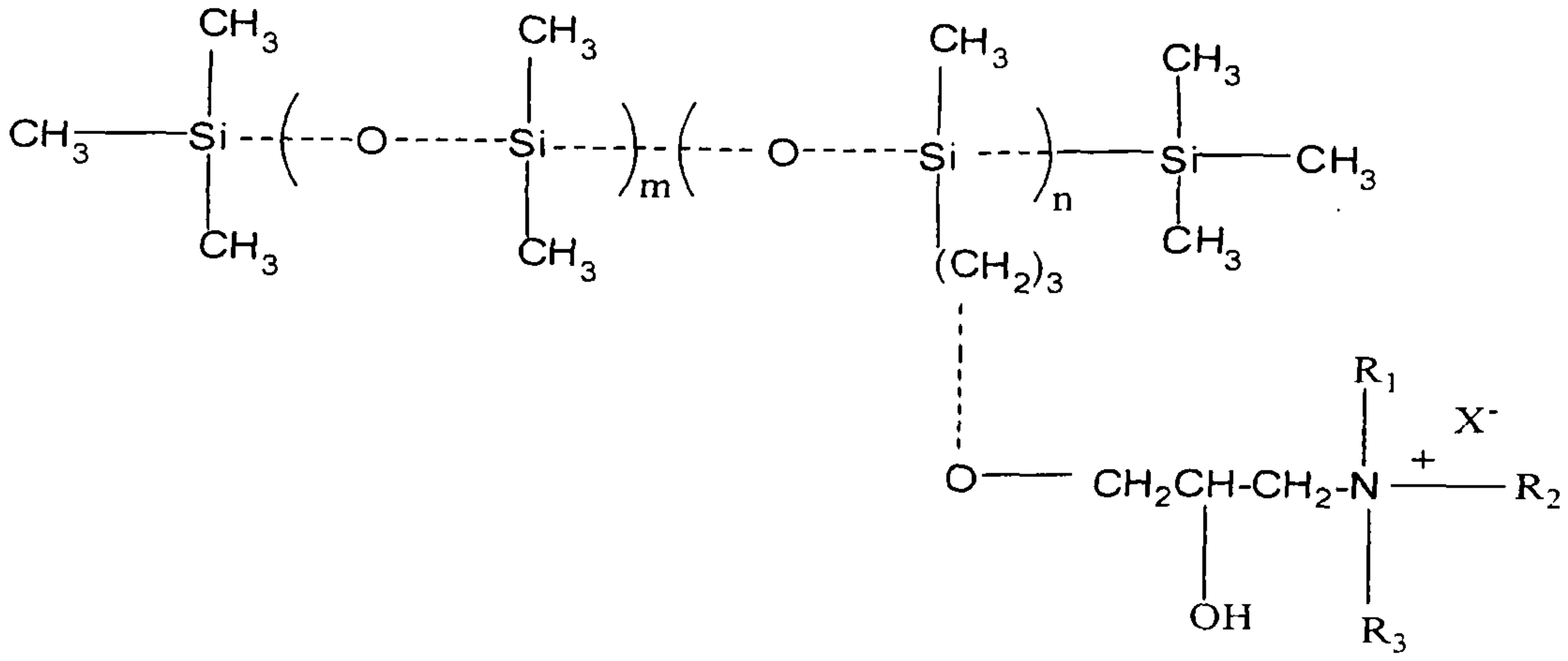
[0024] Any suitable carrier fluid may be used to introduce exemplary embodiments of the cationic polyorganosiloxane into the subterranean formation, including aqueous fluids, non-aqueous fluids, and combinations thereof. Examples of suitable aqueous fluids include fresh water and salt water. As will be appreciated, salt water refers to water containing one or more salts dissolved therein, for example, brines and seawater. Examples of suitable non-aqueous fluids include oxygenated solvents, hydrocarbon solvents, and combinations thereof. Exemplary oxygenated solvents that may be utilized include alcohols, glycols, esters, ethers, and combinations thereof. Specific examples of oxygenated solvents include methanol, ethanol, isopropanol, ethylene glycol, glycerol, ethyleneglycol monomethyl ether, ethyleneglycol monobutyl ether, di-isotridecyl ether and isobutyl oleate ester. Exemplary hydrocarbon solvents that may be utilized include gasoline, kerosene, toluene, xylene, alpha-olefins and mineral oils. Those of ordinary skill in the art will appreciate that, when a combination of an aqueous fluid and a non-aqueous fluid or a combination of a polar (e.g., an alcohol) non-aqueous fluid and a non-polar (e.g., a hydrocarbon) non-aqueous fluid is utilized, an agent may be included therein to facilitate the mixing of the fluids. Moreover, those of ordinary skill in the art should be able to select an appropriate carrier fluid for the cationic polyorganosiloxane based on a number of factors, including well conditions, formation characteristics, solubility of the cationic polyorganosiloxane, and other factors known to those of ordinary skill in the art. For example, in certain embodiments, methanol may be used when treating a coal bed.

[0025] As previously mentioned, exemplary embodiments of the cationic polyorganosiloxane may be introduced into the subterranean formation to increase gas production therefrom. In general, suitable polyorganosiloxanes comprise at least two quaternary ammonium groups. The quaternary ammonium groups may be present on the pendant groups (see Structure 1 below) or at the chain ends of the organosiloxane polymer chains (see Structure 2 below). The number of quaternary groups per chain of the organosiloxane is preferably at least two, and may range from 2 to 150 or from 2 to 70. In some exemplary embodiments, about 10% of silicon atoms in the polymer chain carry quaternary ammonium groups. The molecular weights of the polymers may be in the range of from about 1,000 to about 150,000. In some exemplary embodiments of the present invention, the molecular weights of the polymers may range from about 1,500 to about 50,000.

[0026] While a wide variety of polyorganosiloxanes may be suitable for use with the present technique, an exemplary embodiment of cationic polyorganosiloxane comprises polydimethysiloxane comprising at least two quaternary ammonium groups. Exemplary quaternary ammonium groups may comprise dialkyl methyl quaternary ammonium groups. The alkyl group of the dialkyl methyl quaternary ammonium groups may contain from about 1 to about 18 carbons. Another example of a suitable quaternary ammonium group comprises two hydroxyalkyl groups and a methyl group. Examples of suitable hydroxyalkyl groups include hydroxyethyl and hydroxypropyl groups. One such example is Silquat® 0283A silicone quat, an experimental product from Siltech Corporation which contains methyl dihydroxyethyl quaternary ammonium groups. Another example of suitable quaternary ammonium group comprises amide in one or more of the substituents on the quaternary nitrogen atom (see Structure 3 below). Examples of such materials include Silquat® AC silicone quat and Silquat® AD silicone quat available from SilTech Corporation. In one embodiment, the cationic polyorganosiloxane comprises a polydimethylsiloxane.

Exemplary polydimethylsiloxanes that comprise a dialkyl quaternary ammonium groups are commercially available from Siltech Corporation, Toronto, Ontario, Canada, including Silquat® AO silicone quat, Silquat® D2 silicone quat, Silquat® AO silicone quat, Silquat® J2 silicone quat, and Silquat® J15 silicone quat. The cationic polydimethylsiloxanes from Siltech Corporation are generally provided as 70% by weight active solutions of the cationic polydimethylsiloxane in hexylene glycol, dipropylene glycol or isopropyl alcohol or they may be completely solvent free. The solubility of the polymers in water or organic solvents is generally determined by the number of branching, chain length, polar groups, for example hydroxyl, ester or ether groups on the pendant or chain end groups, and the functional groups attached to the quaternary ammonium nitrogen.

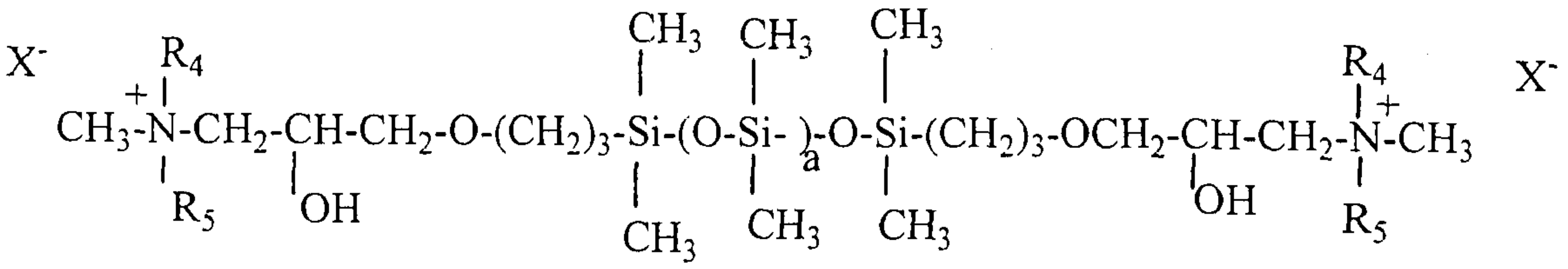
[0027] By way of example, a suitable cationic polydimethylsiloxane comprising at least two quaternary ammonium groups may have the structure shown below:



Structure 1

wherein R_1 and R_2 are independently alkyl groups comprising 1 to 18 carbons, or hydroxyalkyl groups such as hydroxyethyl or hydroxypropyl groups, R_3 is a methyl group, n is an integer in the range of from 2 to 150, m is an integer in the range of from 20 to 2,000, and X^- is a compatible anion, such as fluoride, chloride, bromide, iodide, nitrate, or nitrite.

[0028] By way of example, another suitable polydimethylsiloxane comprising at least two dialkyl quaternary ammonium groups may have the structure shown below:

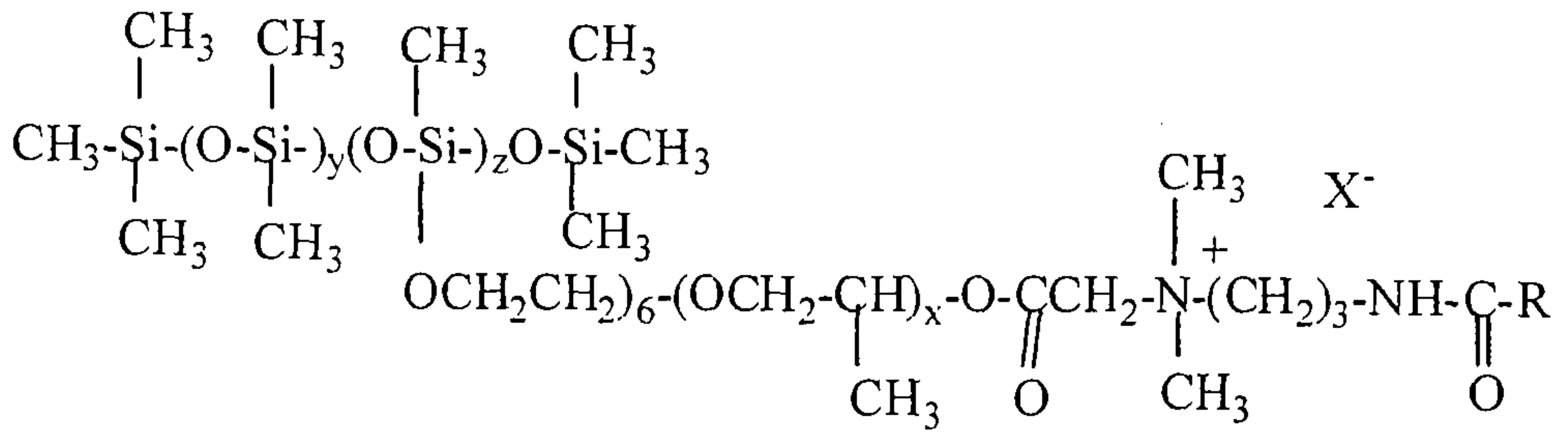


$$X^- \; CH_3\text{-}\overset{R_4}{\underset{R_5}{N^+}}\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}O\text{-}(CH_2)_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_a\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}(CH_2)_3\text{-}OCH_2\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}\overset{R_4}{\underset{R_5}{N^+}}\text{-}CH_3 \; X^-$$

Structure 2

wherein R_4 and R_5 are independently alkyl groups comprising 1 to 18 carbons, or hydroxyalkyl groups such as hydroxyethyl or hydroxypropyl groups, a is an integer in the range of from 10 to 2,000, and X^- is a compatible anion, such as fluoride, chloride, bromide, iodide, nitrate, or nitrite.

[0029] By way of example, another suitable polydimethylsiloxane comprising at least two dialkyl quaternary ammonium groups may have the structure shown below:



$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_y(O\text{-}\overset{CH_3}{\underset{|}{Si}}\text{-})_z O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3$$

$$OCH_2CH_2)_6\text{-}(OCH_2\text{-}\underset{CH_3}{CH})_x\text{-}O\text{-}\underset{O}{\underset{\|}{C}}CH_2\text{-}\overset{CH_3}{\underset{CH_3}{N^+}}\text{-}(CH_2)_3\text{-}NH\text{-}\underset{O}{\underset{\|}{C}}\text{-}R \quad X^-$$

Structure 3

wherein R is an alkyl group comprising 1 to 18 carbons, or a hydroxyalkyl group such as a hydroxyethyl or hydroxypropyl group, x is an integer in the range from 2 to 150, y is an integer in the range of from 10 to 2,000, z is an integer in the range of from 10 to 2,000, and X^- is a compatible anion, such as fluoride, chloride, bromide, iodide, nitrate, or nitrite.

[0030] Exemplary embodiments of the cationic polyorganosiloxane may be present in the treatment fluid in an amount sufficient to provide the desired end result. In an exemplary embodiment of the present invention, the cationic polyorganosiloxane may be present in the treatment fluid in an amount in the range of from about 0.1% to about 10% by weight of the treatment fluid. In certain exemplary embodiments, the cationic polyorganosiloxane may be present in the treatment in an amount in the range of from about 0.5% to about 5% by weight of the treatment fluid.

[0031] Those of ordinary skill in the art will recognize that other additives suitable for use in subterranean treatments may also be included in exemplary embodiments of the treatment fluids of the present invention. Examples of such additives may include corrosion inhibitors, viscosifiers such as polysaccharides and gums, hydrophilic polymers, crosslinking agents, mineral and organic acids, surfactants, particulates such as sand or proppant materials, and combinations thereof.

[0032] As previously mentioned, exemplary embodiments of the polyorganosiloxanes may be used to treat subterranean formations to reduce water blocks therein, thereby improving gas production. An example of a method of treating a subterranean formation to improve gas production therefrom comprises introducing a cationic polyorganosiloxane into the subterranean formation. As previously mentioned, the cationic polyorganosiloxane comprises at least two quaternary ammonium groups. Those of ordinary skill in the art will appreciate that the cationic polyorganosiloxane may be introduced into the formation at any point in the life of the well to achieve the desired end result. By way of example, the cationic polyorganosiloxane may be used in a remedial treatment of a subterranean formation from which gas production rates are less than desired or expected due to, among other things, water blocks. In another example, the cationic polyorganosiloxane may be used to treat a subterranean formation prior to initial gas production therefrom. For example, the cationic polyorganosiloxane may be used to treat the formation after drilling of the well bore, but prior to the well being placed into production. In one example, the cationic polyorganosiloxane may be introduced into the formation in conjunction with another treatment performed in the well bore. For example, the cationic polyorganosiloxane may be included in a treatment fluid (such as a fracturing fluid, completion fluid, etc.) that is introduced into the well bore. In one exemplary embodiment, a fracturing fluid comprising the cationic polyorganosiloxane may be introduced into the subterranean formation at a pressure sufficient to create or enhance one or more fractures in the formation. The fluid comprising the cationic polyorganosiloxane may be introduced prior to or subsequent to fracturing operation. In other words, the cationic polyorganosiloxane may be included in a pre-fracturing fluid referred to as a "prepad" or it may be part of a fluid that immediately follows the fracturing fluid.

[0033] To facilitate a better understanding of the present technique, the following examples of some specific embodiments are given. In no way should the following examples be read to limit, or to define, the scope of the invention.

EXAMPLE 1

[0034] A series of tests was performed to analyze the effects of a variety of materials on the water-imbibition and water-drainage rates of sandstone cores with a hydrocarbon as the carrier fluid. In each of these tests, the treatment fluid comprised 1.0% wt/vol of the tested material in kerosene. For a control, tests were also performed with only the kerosene itself.

[0035] These tests were performed using high permeability (200-300 millidarcy) Berea sandstone cores in accordance with the following procedure. The Berea sandstone cores measured about 1 inch in diameter and about 2.8-3.3 inches in length. First, a dry core was vacuum saturated with the treatment fluid for two hours by submerging the dry core in the test fluid placed in a loosely capped container that is kept in a vacuum chamber. It was determined that the core was fully saturated with the treatment fluid when no air bubbles could be seen exiting the core. The core was then weighed to determine the saturated core weight. Using the density of the carrier fluid, the pore volume of the core was determined based on the difference between the saturated core weight and the unsaturated core weight.

[0036] Next, the saturated core was wrapped along its length in a plastic film and placed into a suction flask assembly. Once the saturated core was placed in the suction flask assembly, the saturated core was subjected to lab vacuum at both ends, until no more fluid came through the core (about 30 minutes). The core was then removed from the suction flask assembly and weighed. Using the density of the carrier fluid, the residual oil saturation (S_{or}) of the core was determined based on the difference between the saturated core weight and the weight after the lab vacuum treatment. The S_{or} is representative of the drainage rate for the core after treatment. From this data, the pore volume occupied by the residual carrier fluid and the unoccupied pore volume were determined.

[0037] Thereafter, the core was placed in 10 milliliters of a 7% potassium chloride solution in a small cup such that the entire surface of one end of the core was exposed to the brine to facilitate brine imbibition. After 10 minutes of exposure to the brine, the core was again weighed. Based on the difference between the weight of the core after brine exposure and the weight of the core after the lab vacuum treatment, the volume of the brine imbibed into the core can be determined. By dividing the volume of the imbibed brine and the unoccupied pore volume, a percent value for brine imbibition into available porosity was calculated.

[0038] The percent brine imbibition into available porosity for each of the tested materials is shown in Table 1 below and is also shown in FIG. 1. The residual oil saturation (% S_{or}) for each of the tested materials is also shown on Table 1 below. As will be appreciated, the drainage rates (represented by the percent S_{or}) for this series of tests are less relevant because they are not for a water-based fluid and do not indicate how the tested materials would effect drainage rates of a water-based fluid.

[0039] After the brine-imbibition tests were completed, a drop of water was placed on one end of the core and the time needed for the absorption of the water droplet into the core was estimated. The values of these measurements are given in Table 1 below and are expected to be a reflection of the oil-wet nature of the treated surface. If the droplet of water took longer to become absorbed, it retained its shape for longer periods indicating contact angles reflective of increased oil-wet nature of the treated surface.

TABLE 1
Kerosene-Based Treatments

Material	Chemical Description	Supplier	% S_{or}	% Brine Imbibition into Available Porosity	Time for Water drop Absorption, minutes
Kerosene (Test #1)	--	--	54.0	43.0	1-2
Kerosene (Test #2)	--	--	55.0	42.0	1-2
EZ MUL®NT emulsifier	Polyaminated fatty acid	Halliburton Energy Services, Inc.	58.1	22.3	>5

INVERMUL® emulsifier	Blend of oxidized tall oil and polyaminated fatty acid	Halliburton Energy Services, Inc.	55.0	16.6	>5
LE SUPERMUL™ emulsion stabilizer	Polyaminated fatty acid	Halliburton Energy Services, Inc.	69.5	17.0	1-5
EZ MUL® additive	Polyaminated fatty acid	Halliburton Energy Services, Inc.	67.9	18.6	1-5
MOC-A™ surfactant	Dodecylbenzenesulfonate salt	Halliburton Energy Services, Inc.	56.2	33.6	immediate
DOC-3™ surfactant	Substituted Imidazoline from condensation of polyamine with a fatty acid	Halliburton Energy Services, Inc.	57.6	29.2	immediate
Span®85 surfactant	Sorbitan trioleate	Aldrich Chem. Co.	57.1	40.0	1-2
DRILTREAT® additive	Lechithin dispersion	Halliburton Energy Services, Inc.	62.8	23.0	1-2
Experimental Product - Silquat® 0283A silicone quat	Oil-soluble PDMS with quaternary ammonium chain end without long chain alkyl groups	Siltech Corp.	54.0	4.28	>20
Experimental Product - Silquat® 0283B silicone quat	Oil-soluble PDMS with quaternary ammonium chain end with two long chain alkyl groups	Siltech Corp.	56.4	-0.03	5-10
Experimental product – Silquat® 0283C silicone quat	Oil-soluble PDMS with quaternary ammonium chain end with long chain alkyl groups	Siltech Corp.	57.0	26.0	<1
Experimental product – Silquat® 0283D silicone quat	Oil-soluble PDMS with quaternary ammonium chain end without long chain alkyl groups	Siltech Corp.	62.3	35.2	<1
Silquat® AO silicone quat	Water-soluble organomodified PDMS silicone with dialkylmethyl quaternary ammonium chain end	Siltech Corp.	60.7	37.0	<10 sec
Silquat® J208-1B silicone quat	Water-soluble organomodified PDMS silicone with dialkylmethyl quaternary ammonium chain end	Siltech Corp.	57.8	43.7	<10 sec

Silquat® D2 silicone quat	Water-soluble organomodified PDMS silicone with dialkylquaternary ammonium chain end	Siltech Corp.	57.3	45.4	<10 sec
Silquat® J2 silicone quat	Water-soluble organomodified PDMS silicone with dialkylmethyl quaternary ammonium chain end	Siltech Corp.	55.1	45.6	<10 sec
OMC® 2 oil mud conditioner	Oligomeric fatty acid	Halliburton Energy Services, Inc.	53.8	41.4	5-10

[0040] The results for this series of tests indicate that the brine-imbibition rates are lower for certain of these cationic polyorganosiloxanes. It is believed that a lower brine-imbibition rate indicates that the core wettability has been modified to a less water-wet condition, which is consistent with the increased time period observed for the water drops to be absorbed into the core. The latter observation is also consistent with increased contact angles (not measured) due to the less-water wetting core surface. Moreover, contact angle data for the core surface were the highest for the materials with the lowest brine-imbibition rates, except for the OMC®2 oil mud conditioner. Accordingly, this result suggests that materials that provide lower brine-imbibition rates are characterized by their ability to modify the core surface to have higher contact angles for the water-to-formation interface.

EXAMPLE 2

[0041] An additional series of tests was performed to further analyze the effects of a variety of materials on the water-imbibition and water-drainage rates of sandstone cores using a water-based carrier fluid. The treatment fluids used in this series of tests comprised 1.0% wt/vol of the tested material in a 7% potassium chloride solution, except for HPT™-1 chemical additive, which was used in an amount of 0.2% wt/vol. For a control, tests were also performed with only the potassium chloride solution itself.

[0042] These tests were performed using high permeability (200-300 millidarcy) Berea sandstone cores in accordance with the following procedure. The Berea sandstone cores measured about 1 inch in diameter and about 2.8-3.3 inches in length. First, a dry core was vacuum saturated with the treatment fluid for four hours. It was determined that the core was fully saturated with the treatment fluid when no air bubbles could be seen exiting the core. The core was then weighed to determine the saturated core weight. Using the density of the carrier fluid, the pore volume of the core was determined based on the difference between the saturated core weight and the unsaturated core weight.

[0043] Next, the saturated core was centrifuged for 20 hours on each end at 1,440 rpm. The core was then removed from the centrifuge and weighed. Using the density of the carrier fluid, the residual water saturation (S_{wr}) of the core was determined based on the difference between saturated core weight and the weight after the centrifuge treatment. The % S_{wr} for this first water-drainage test is shown below in Table 2 as well as on FIGS. 2 and 3. The residual water saturation is representative of the water-drainage rate for the core after treatment. From this data, the pore volume occupied by the residual treatment fluid and the unoccupied pore volume were determined.

[0044] Thereafter, the core was placed in 10 milliliters of a 7% potassium chloride solution in a small cup such that the entire surface of one end of the core was exposed to the brine to facilitate brine imbibition. This entire assembly was placed into a closed bottle. After two hours of exposure to the brine, the core was again weighed. Based on the difference between the weight of the core after brine exposure and the weight of the core after the centrifuge treatment, the volume of the brine imbibed into the core can be determined. By dividing the volume of the imbibed brine and the unoccupied pore volume, a percent value for brine imbibition into available porosity was calculated. The % brine imbibition for this test is shown below in Table 2 as well as on FIG. 3.

[0045] After the brine-imbibition test, a second water-drainage test was performed on the core. The core was immersed in 100 milliliters of a 7% sodium chloride solution and subjected to vacuum for three hours. Then, the core was centrifuged at 1,440 rpm, and the water-drainage rate was calculated as a function of time over a period of 21 hours to provide dynamic-water-drainage results. Measurements of the core weight were taken periodically by removing the core from the centrifuge. A final measurement of the core weight was recorded after 21 hours. From these measurements, the percent S_{wr} was determined as described above. The final percent S_{wr} for this second water-drainage test is shown below in Table 2 as well as on FIG. 2. In addition, the dynamic water-drainage results are provided on FIG. 4 as percent S_{wr} as a function of time.

[0046] As previously mentioned, the percent S_{wr} for the first water-drainage test, the percent S_{wr} for the second water-drainage tests, and the percent brine imbibition for each of the tested materials are shown in Table 2 below. As previously mentioned, the percent S_{wr} represents the water-drainage rate.

TABLE 2
Brine-Based Treatments

Material	Chemical Description	Supplier	% S_{WT} (1^{st} Drainage Test)	% S_{WT} (2^{nd} Drainage Test)	% Brine Imbibition
7% KCl	--	--	20.2	21.1	47.1
Silquat® D2 silicone quat	Water-soluble organomodified PDMS silicone with dialkylquaternary ammonium chain end	Siltech Corp.	14.5	16.0	43.9
Arquad® DMCB-80	Cocobenzyldimethylammonium chloride	Akzo Nobel	20.8	25.5	50.6
Silquat® AO silicone quat	Water-soluble organomodified PDMS silicone with dialkylquaternary ammonium chain end	Siltech Corp.	16.3	16.7	38.7
Silquat® J2 silicone quat	Water-soluble organomodified PDMS silicone with dialkylquaternary ammonium chain end	Siltech Corp.	16.6	16.9	39.6
Silquat® J208-1B silicone quat	Water-soluble organomodified PDMS silicone with dialkylquaternary ammonium chain end	Siltech Corp.	13.4	16.6	45.4
CTAB	Cetyltrimethylammonium bromide	Aldrich Chem. Co.	23.4	26.7	48.9
HPT™ -1 additive	Hydrophobically modified water soluble poly-(dimethylaminoethylmethacrylate)	Halliburton Energy Services, Inc.	25.9	31.1	43.0

[0047] The results of this series of tests show that the water-drainage rates (represented by the S_{wr}) are consistently lower for the cationic polyorganosiloxanes that comprise at least two cationic quaternary ammonium groups when compared to the other materials tested. As illustrated by the dynamic-water-drainage rates shown in FIG. 4, the four cationic polyorganosiloxanes tested have the fastest water-drainage rates. Regarding water imbibition, this series of tests also indicates that the water-imbibition rates of the cores treated with the cationic polyorganosiloxanes had lower values than other materials tested. In addition, it was surprisingly found that the percent brine imbibition increased for quaternary ammonium surfactants without the silicon-based structure, such as for the CTAB and the Arquad® DMBCB-80. This observation indicates, use of monomeric quaternary ammonium salts with long alkyl chains is not sufficient to lower the imbibition rates. They need to be part of a polyorganosiloxane polymer chain to be effective in lowering the imbibition rates.

EXAMPLE 3

[0048] An additional series of tests was performed to further analyze the effects of a variety of materials on the water-imbibition and water-drainage rates of sandstone cores. The treatment fluids used in this series of tests comprised 1.0% wt/vol of the tested material in methanol, except for HPT™-1 chemical additive, which was used in an amount of 0.2% wt/vol. For a control, tests were also performed with only methanol itself.

[0049] These tests were performed using high permeability (200-300 millidarcy) Berea sandstone cores in accordance with the following procedure. The Berea sandstone cores measured about 1 inch in diameter and about 2.8-3.3 inches in length. First, a dry core was vacuum saturated with the treatment fluid for two hours. It was determined that the core was fully saturated with the treatment fluid when no air bubbles could be seen exiting the core. The core was then weighed to determine the saturated core weight. Using the density of the carrier fluid, the pore volume of the core was determined based on the difference between the saturated core weight and the unsaturated core weight. The core was then allowed to sit at ambient temperature and pressure overnight.

[0050] Next, the saturated core was centrifuged alternately for 10 minutes on each end for a total of 40 minutes per core at 1,440 rpm. The core was then removed from the centrifuge and weighed. Using the density of the carrier fluid, the residual methanol saturation (S_{mr}) of the core was determined based on the difference between saturated core weight and the weight after the centrifuge treatment. The % S_{mr} for this first drainage test is shown below in Table 3. The residual methanol saturation is representative of the drainage rate for the core after treatment. From this data, the pore volume occupied by the residual treatment fluid and the unoccupied pore volume were determined.

[0051] Thereafter, the core was placed in 10 milliliters of a 7% potassium chloride solution in a small cup such that the entire surface of one end of the core was exposed to the brine to facilitate brine imbibition. This entire assembly was placed into a closed bottle.

After 10 minutes of exposure to the brine, the core was again weighed. Based on the difference between the weight of the core after brine exposure and the weight of the core after the centrifuge treatment, the volume of the brine imbibed into the core can be determined. By dividing the volume of the imbibed brine and the unoccupied pore volume, a percent value for brine imbibition into available porosity was calculated. The % brine imbibition for this test is shown below in Table 3 as well as in FIGS. 5 and 6.

[0052] After the brine-imbibition test, another water-drainage test was performed on the core. The core was immersed in 100 milliliters of a 7% potassium chloride solution and subjected to vacuum for three hours. Then, the core was centrifuged at 1,440 rpm, and the water-drainage rate was calculated as a function of time over a period of 22 hours to provide dynamic-water-drainage results. Measurements of the core weight were taken periodically by removing the core from the centrifuge. A final measurement of the core weight was recorded after 22 hours. From these measurements, the percent S_{wr} was determined as described above. The final percent S_{wr} for this second drainage test is shown below in Table 3. In addition, the dynamic water-drainage results are provided on FIG. 7 as percent S_{wr} as a function of time.

[0053] As previously mentioned, the percent S_{mr} for the first drainage test, the percent S_{wr} for the second drainage test, and the percent brine imbibition for each of the tested materials are shown in Table 3 below. As will be appreciated, the drainage rates (represented by the percent S_{mr}) for the first drainage tests are less relevant because they are not for a water-based fluid and do not indicate how the tested materials would effect drainage rates of a water-based fluid.

TABLE 3
Methanol-Based Treatments

Material	Chemical Description	Supplier	% S_{mr} (first drainage test)	% S_{wr} (second drainage test)	% Brine Imbibition
Methanol	--	--	21.7	n.d.	27.8
CTAB	Cetyltrimethylammonium bromide	Aldrich Chem. Co.	23.9	n.d.	26.6
Silquat®D2 silicone quat	Water soluble organomodified PDMS silicone with dialkylquaternary ammonium chain end	Siltech Corp.	22.0	n.d.	27.7
Silquat®AO silicone quat	Water soluble organomodified PDMS silicone with dialkylquaternary ammonium chain end	Siltech Corp.	23.6	n.d.	29.0
Experimental Product - Silquat 0283®A silicone quat	Oil-soluble PDMS with quaternary ammonium chain end without long chain alkyl groups	Siltech Corp.	20.9	n.d.	-1.7
Silquat®J15 silicone quat	Water-soluble organomodified PDMS silicone with dialkylquaternary ammonium chain end	Siltech Corp.	21.1	n.d.	6.8
EZ MUL®NT emulsifier	Polyaminated fatty acid	Halliburton Energy Services, Inc.	23.7	n.d.	29.3
FC 4430	Non-ionic polymeric fluorocarbon compound	3M Corporation	27.3	n.d.	26.9
ENWAR™ 288 additive	Cationic fluorocarbon	Halliburton Energy Services, Inc.	15.5	n.d.	38.3
SuperFlo™ surfactant	Nonionic fluorocarbon surfactant blend	Halliburton Energy Services, Inc.	16.2	n.d.	39.2
Pen™ 88 additive	Nonylphenol ethoxylate	Halliburton Energy Services, Inc.	24.5	n.d.	42.1
Zonyl®FS-500 fluoro additive	Non-ionic fluoroaklyl compound	Dupont	17.5	n.d.	26.2

HPT™-1 chemical additive	Hydrophobically modified water soluble poly-(dimethylaminoethylmethacrylate)	Halliburton Energy Services, Inc.	20.9	n.d.	25.7
Methanol	--	--	18.7	18.5	39.5
Silquat®J15 silicone quat	Water-soluble organomodified PDMS silicone with dialkylquaternary ammonium chain end		23.7		20.6
Experimental Product - Silquat 0283®A silicone quat	Oil soluble PDMS with quaternary ammonium chain end without long chain alkyl groups	Siltech Corp.	20.7	13.7	3.0
SSO-21M	Non-ionic surfactant blend	Halliburton Energy Services, Inc.	27.3	n.d.	20.5
GasPerm™ 1000	Non-ionic surfactant blend	Halliburton Energy Services, Inc.	23.0	14.8	34.6
Tegotop® 105 agent	Highly disperse silicon dioxide nano-particles in silicone wax and cyclomethicone	Degussa AG	21.7	n.d.	39.5
Tego® Polish	Methylpolysiloxane	Degussa AG	21.7	n.d.	41.2
Tegotop® 105 agent + Tego® Polish	Highly disperse silicon dioxide nano-particles in silicone wax and cyclomethicone plus Methylpolysiloxane	Degussa AG	23.4	21.9	22.5
Tego® Polish followed by Tegotop® 105 agent	Methylpolysiloxane followed by Highly disperse silicon dioxide nano-particles in silicone wax and cyclomethicone	Degussa AG	21.8	n.d.	30.7
Tegotop® 105 agent followed by Tego® Polish	Highly disperse silicon dioxide nano-particles in silicone wax and cyclomethicone followed by Methylpolysiloxane	Degussa AG	19.4	n.d.	36.4
Tegopren® 6921 agent	Diquaternary polydimethylsiloxane in propanediol	Degussa AG	23.3	n.d.	35.7
Tegosivin® HL100 agent	Methylethoxy polysiloxane	Degussa AG	24.9	n.d.	37.0
Tegosivin® HE328 agent	Silane/Siloxanes emulsion	Degussa AG	26.3	n.d.	35.4
Tegopren® 6922 agent	Diquaternary polydimethylsiloxane	Degussa AG	24.7	n.d.	33.6

Repell 2111 agent	Triethoxy (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecatluorooctyl) silane	Degussa AG	22.8	n.d.	37.6

[0054] The results of this series of tests show that the brine-imbibition rates for the cores are consistently lower for the polyorganosiloxanes that comprise at least two quaternary ammonium groups when compared to the other materials tested. Surprisingly, these polyorganosiloxanes exhlbited superior imbibition rates even when compared to the fluoro polymer-based materials tested, such as the FC 4430, ENWAR® 288 additive, and the SuperFlo™ surfactant, which are expected to have high interfacial surface tension reduction in addition to increasing contact angles.

CLAIMS

1. A treatment fluid for treating a subterranean formation to improve gas production therefrom, the treatment fluid comprising: a non-aqueous fluid and an oil-soluble cationic polydimethylsiloxane, the cationic polydimethylsiloxane comprising at least two cationic quaternary ammonium groups, wherein the quaternary ammonium groups are present on one or more pendant groups of the polydimethylsiloxane or on one or more chain ends of the polydimethylsiloxane.

2. The treatment fluid of claim 1, wherein at least one of the quaternary ammonium groups comprises a dialkyl methyl quaternary ammonium group.

3. The treatment fluid of claim 1, wherein at least one of the quaternary ammonium groups comprises two hydroxyalkyl groups and a methyl group.

4. The treatment fluid of claim 1, wherein at least one of the quaternary ammonium groups comprises amide in one or more of the substituents on a quaternary nitrogen atom of the quaternary ammonium group.

5. A treatment fluid for treating a subterranean formation to improve gas production therefrom, the treatment fluid comprising: an aqueous fluid and a water-soluble cationic polydimethylsiloxane, the cationic polydimethylsiloxane comprising at least two cationic quaternary ammonium groups.

6. The treatment fluid of claim 5, wherein the quaternary ammonium groups are present on one or more pendant groups of the polydimethylsiloxane or on one or more chain ends of the polydimethylsiloxane.

7. The treatment fluid of claim 5, wherein at least one of the quaternary ammonium groups comprises a dialkyl methyl quaternary ammonium group.

8. The treatment fluid of claim 5, wherein at least one of the quaternary ammonium groups comprises two hydroxyalkyl groups and a methyl group.

9. The treatment fluid of claim 5, wherein at least one of the quaternary ammonium groups comprises amide in one or more of the substituents on a quaternary nitrogen atom of the quaternary ammonium group.

10. The treatment fluid of claim 5, wherein the aqueous fluid comprises at least one fluid selected from the group consisting of fresh water, salt water, and combinations thereof.

11. A method of treating a subterranean formation to improve gas production therefrom, the method comprising:

introducing a cationic polyorganosiloxane into the subterranean formation, wherein the cationic polyorganosiloxane comprises at least two quaternary ammonium groups, wherein the quaternary ammonium groups are present on one or more pendant groups of the polyorganosiloxane or on one or more chain ends of the polyorganosiloxane.

12. The method of claim 11, further comprising producing gas from the subterranean formation.

13. The method of claim 11, wherein gas has been produced from the subterranean formation prior to introducing the cationic polyorganosiloxane into the subterranean formation.

14. The method of claim 11, wherein introducing the cationic polyorganosiloxane into the subterranean formation increases the contact angle between water and one or more formation surfaces.

15. The method of claim 11, wherein in the range of from 2 to 150 quaternary ammonium groups are present per chain of the organosiloxane in the polyorganosiloxane.

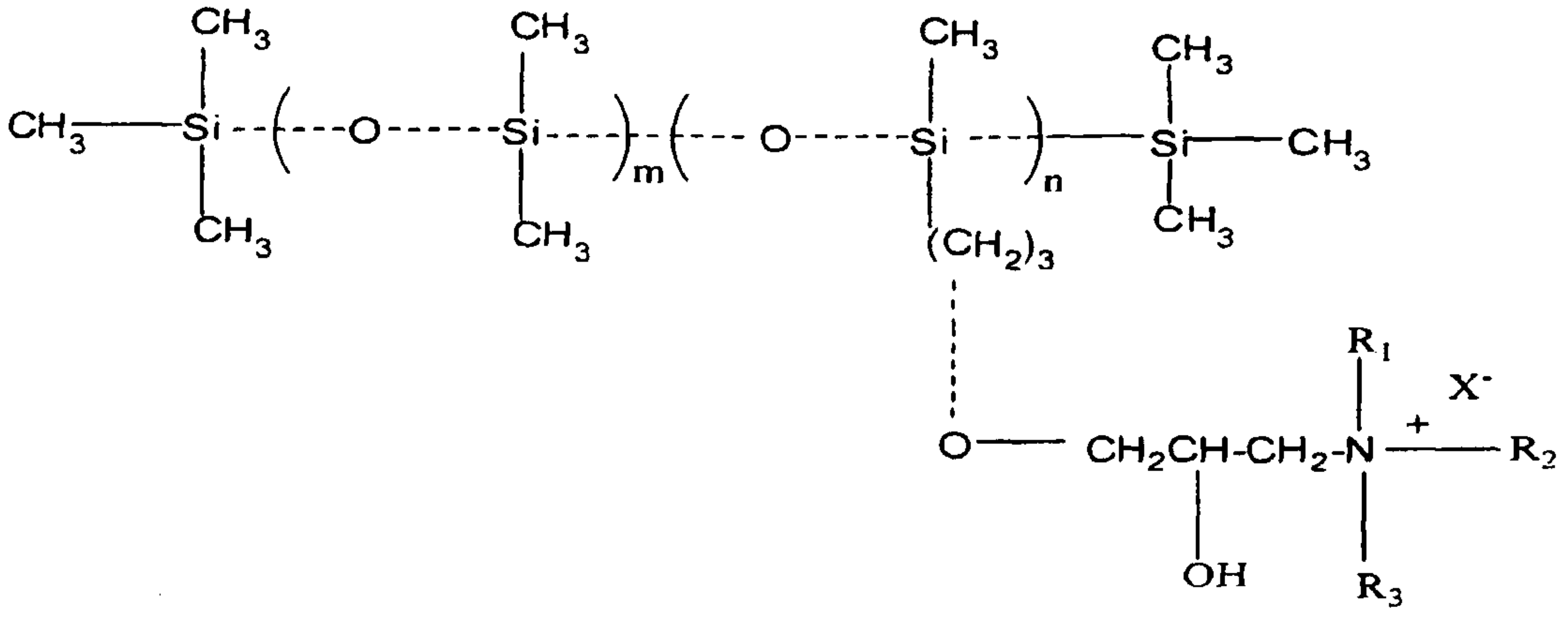
16. The method of claim 11, wherein the cationic polyorganosiloxane comprises a polydimethylsiloxane comprising at least two quaternary ammonium groups.

17. The method of claim 11, wherein at least one of the quaternary ammonium groups comprises a dialkyl methyl quaternary ammonium group.

18. The method of claim 11, wherein at least one of the quaternary ammonium groups comprises two hydroxyalkyl groups and a methyl group.

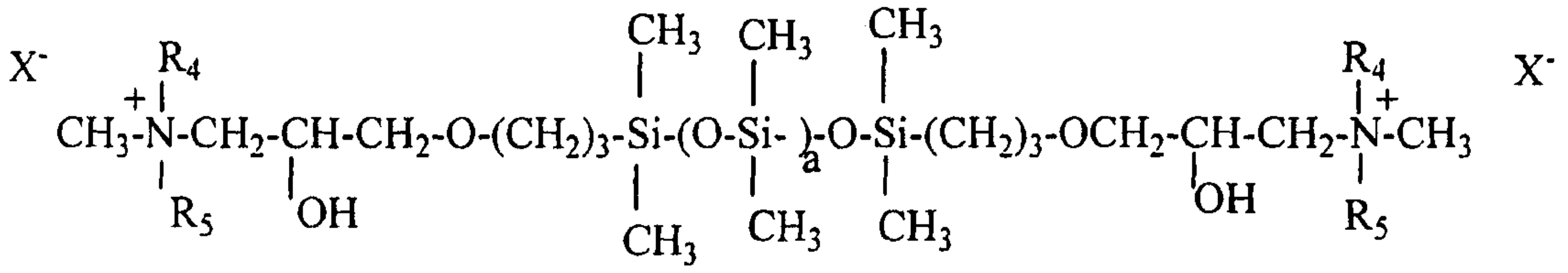
19. The method of claim 11, wherein at least one of the quaternary ammonium groups comprises amide in one or more of the substituents on a quaternary nitrogen atom of the quaternary ammonium group.

20. The method of claim 11, wherein the cationic polyorganosiloxane is represented by the following structure:



wherein R_1 is an alkyl group comprising 1 to 18 carbons, or a hydroxyalkyl group, R_2 is an alkyl group comprising 1 to 18 carbons, or a hydroxyalkyl group, R_3 is a methyl group, n is an integer in the range of from 2 to 150, m is an integer in the range of from 20 to 2,000, and X· is a compatible anion.

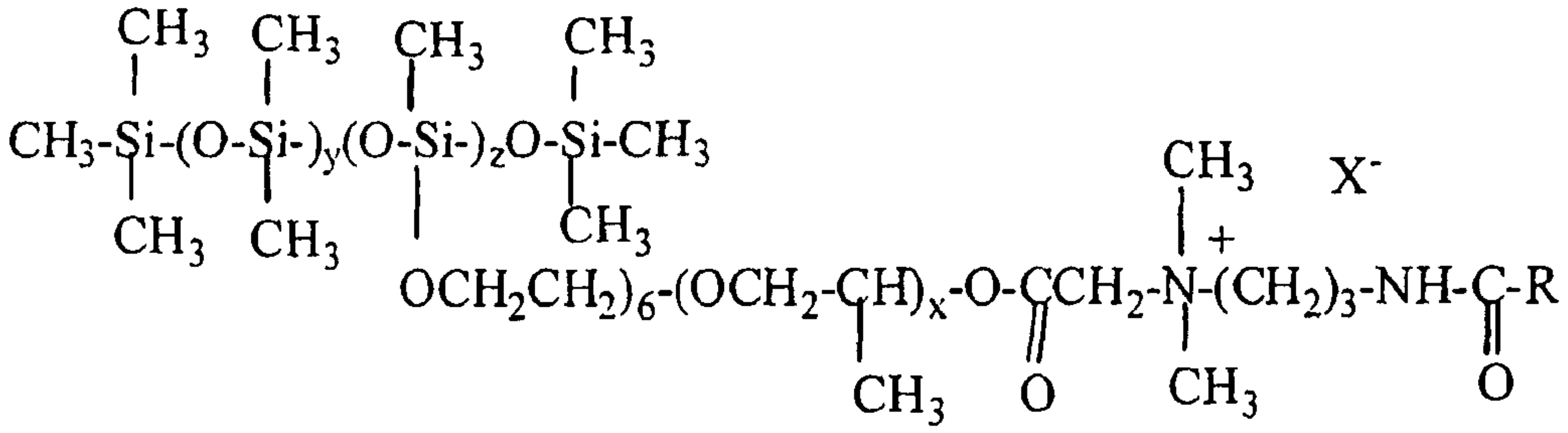
21. The method of claim 11, wherein the cationic polyorganosiloxane is represented by the following structure:



$$X^- \; CH_3\text{-}\overset{R_4}{\underset{R_5}{\overset{+}{N}}}\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}O\text{-}(CH_2)_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_a\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}(CH_2)_3\text{-}OCH_2\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}\overset{R_4}{\underset{R_5}{\overset{+}{N}}}\text{-}CH_3 \; X^-$$

wherein R_4 is an alkyl group comprising 1 to 18 carbons, or a hydroxyalkyl group, R_5 is an alkyl group comprising 1 to 18 carbons, or a hydroxyalkyl group, a is an integer in the range of from 10 to 2,000, and X· is a compatible anion.

22. The method of claim 11, wherein the cationic polyorganosiloxane is represented by the following structure:



$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_y(O\text{-}\overset{CH_3}{\underset{|}{Si}}\text{-})_zO\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_3$$

$$OCH_2CH_2)_6\text{-}(OCH_2\text{-}\underset{CH_3}{CH})_x\text{-}O\text{-}\underset{O}{C}CH_2\text{-}\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}\text{-}(CH_2)_3\text{-}NH\text{-}\underset{O}{C}\text{-}R \quad X^-$$

wherein R is an alkyl group comprising 1 to 18 carbons, or a hydroxyalkyl group, x is integer in the range from 2 to 150, y is an integer in the range of from 10 to 2,000, z is an integer in the range of from 10 to 2,000, and X is a compatible anion.

23. The method of claim 11, wherein introducing the cationic polyorganosiloxane into the subterranean formation comprises introducing a treatment fluid into the formation, wherein the treatment fluid comprises a base fluid and wherein the cationic polyorganosiloxane is present in the treatment fluid in an amount in the range of from about 0.1% to about 10% by weight of the treatment fluid.

24. The method of claim 23, wherein the treatment fluid is introduced into the formation at or above a pressure sufficient to create or enhance one or more fractures in the subterranean formation.

25. The method of claim 11, further comprising introducing a fracturing fluid into the subterranean formation at or above a pressure sufficient to create or enhance one or more fractures in the subterranean formation.

26. A method comprising:

providing a treatment fluid comprising: a non-aqueous fluid and a cationic polyorganosiloxane comprising at least two quaternary ammonium groups, wherein the cationic polyorganosiloxane is present in an amount in the range of from 0.1% to 10% by the combined weight of the non-aqueous fluid and the cationic polyorganosiloxane; and

placing the treatment fluid in a portion of a subterranean formation.

27. The method of claim 26 further comprising producing gas from the subterranean formation.

28. The method of claim 27 wherein in the range of from 2 to 150 quaternary ammonium groups are present per chain of the organosiloxane in the polyorganosiloxane.

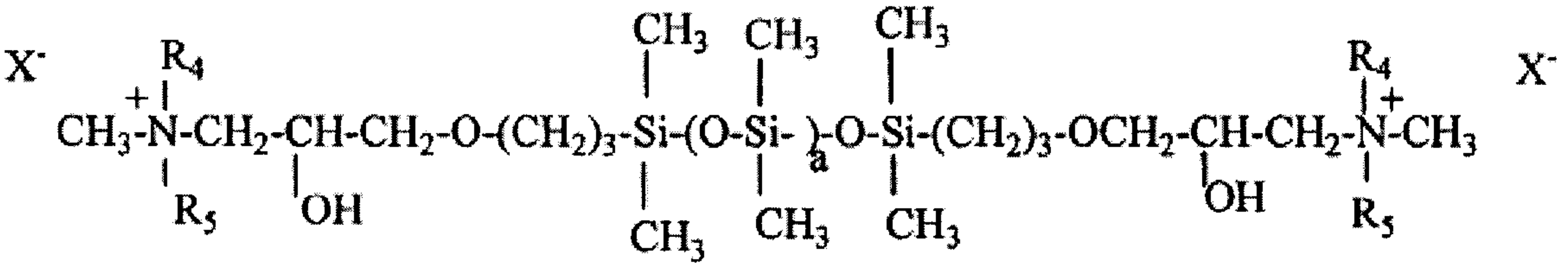
29. The method of claim 26 wherein the cationic polyorganosiloxane comprises a polydimethylsiloxane comprising at least two quaternary ammonium groups.

30. The method of claim 26 wherein at least one of the quaternary ammonium groups comprises a dialkyl methyl quaternary ammonium group.

31. The method of claim 26 wherein at least one of the quaternary ammonium groups comprises two hydroxyalkyl groups and a methyl group.

32. The method of claim 26 wherein at least one of the quaternary ammonium groups comprises amide in one or more of the substituents on a quaternary nitrogen atom of the quaternary ammonium group.

33. The method of claim 26 wherein the cationic polyorganosiloxane comprises a compound represented by the following structure:



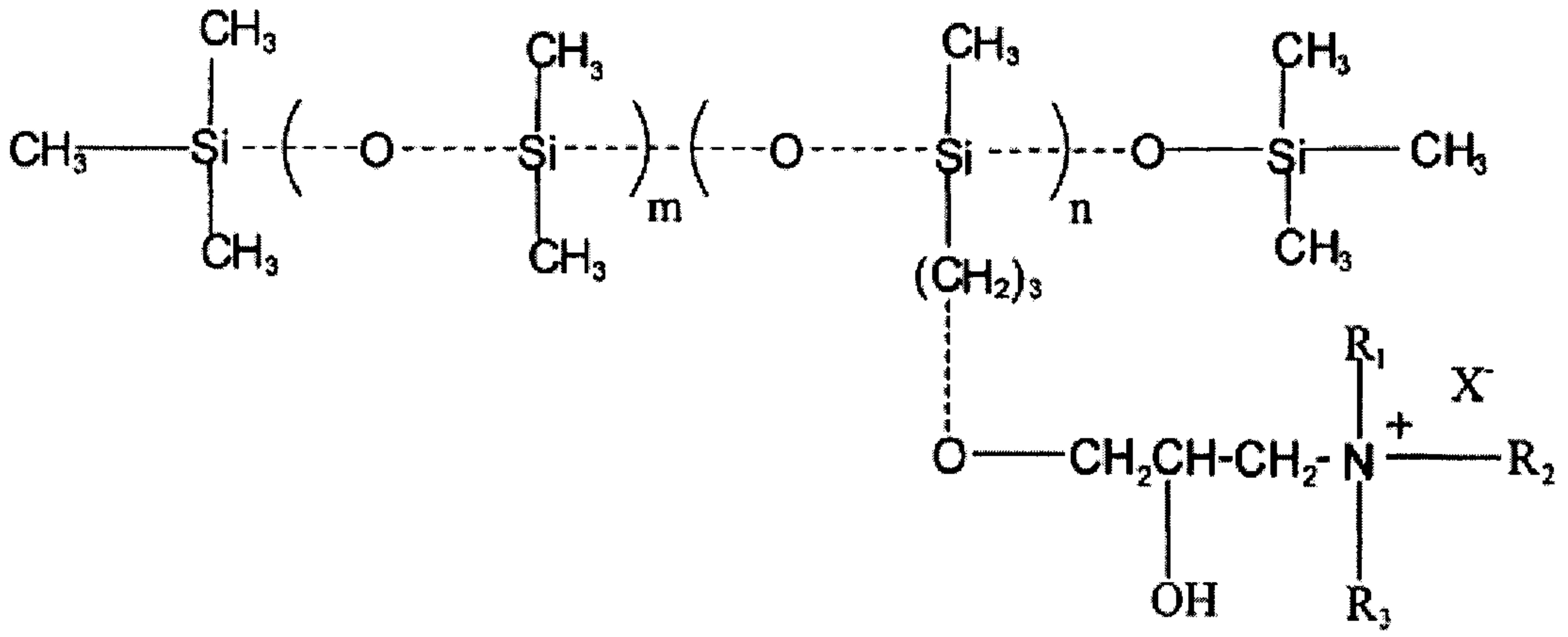
$$X^- \quad CH_3\text{-}\overset{R_4}{\underset{R_5}{\overset{+}{N}}}\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}O\text{-}(CH_2)_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}(O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-})_a\text{-}O\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}(CH_2)_3\text{-}OCH_2\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}\overset{R_4}{\underset{R_5}{\overset{+}{N}}}\text{-}CH_3 \quad X^-$$

wherein R_4 is an alkyl group comprising 1 to 18 carbons, or a hydroxyalkyl group, R_5 is an alkyl group comprising 1 to 18 carbons, or a hydroxyalkyl group, a is an integer in the range of from 10 to 2,000, and X^- is a compatible anion.

34. The method of claim 26 wherein the treatment fluid is introduced into the formation at or above a pressure sufficient to create or enhance one or more fractures in the subterranean formation.

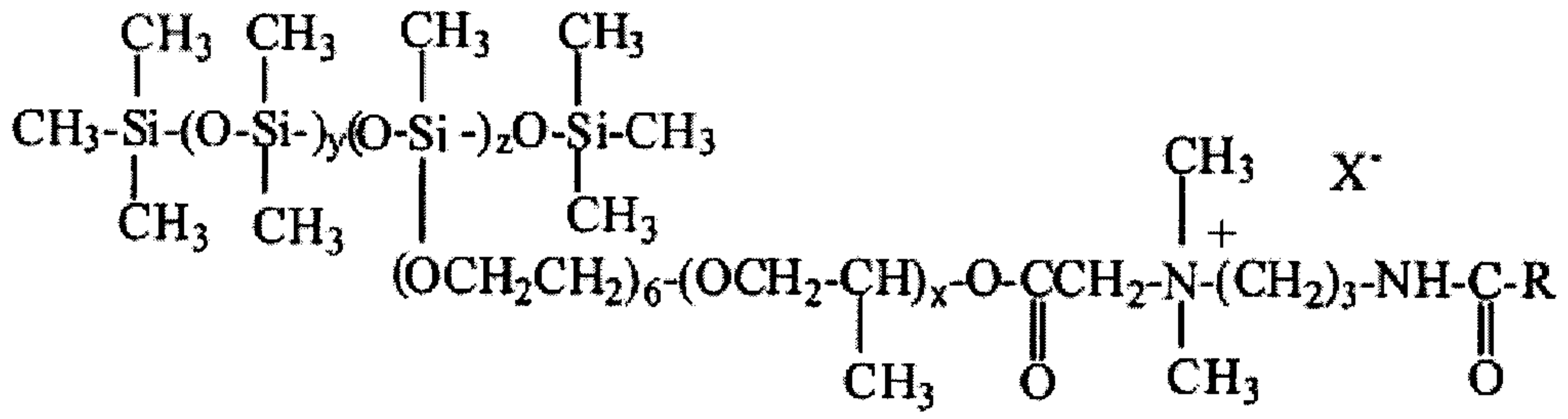
35. The method of claim 26 wherein the cationic polyorganosiloxane is present in the treatment fluid in an amount in the range of from 0.5% to 5% by the combined weight of the non-aqueous fluid and the cationic polyorganosiloxane.

36. The method of claim 26 wherein the cationic polyorganosiloxane comprises a compound represented by the following structure:



wherein R_1 is an alkyl group comprising 1 to 18 carbons, or a hydroxyalkyl group, R_2 is an alkyl group comprising 1 to 18 carbons, or a hydroxyalkyl group, R_3 is a methyl group, n is an integer in the range of from 2 to 150, m is an integer in the range of from 20 to 2,000, and X^- is a compatible anion.

37. The method of claim 26 wherein the cationic polyorganosiloxane comprises a compound represented by the following structure:



wherein R is an alkyl group comprising 1 to 18 carbons, or a hydroxyalkyl group, x is integer in the range from 2 to 150, y is an integer in the range of from 10 to 2,000, z is an integer in the range of from 10 to 2,000, and X^- is a compatible anion.

38. The method of claim 26 further comprising:

allowing the polyorganosiloxane to interact with water present in the subterranean formation, a surface of the formation, or any combination thereof so as to increase the contact angle between the water and the formation surface; and allowing the water drainage rate of the portion of the formation to increase.

39. The method of claim 26 further comprising:

allowing the polyorganosiloxane to interact with the portion of the subterranean formation to reduce the tendency of the portion to imbibe water in at least one gas flow channel present in the subterranean formation.

40. The method of claim 26 further comprising:

allowing the polyorganosiloxane to interact with the portion of the subterranean formation so as to reduce the tendency of the formation to imbibe water.

Fig.1.

Water Imbibition Into Treated Berea Cores
% Brine Imbibition v. Pre-Treat Solution

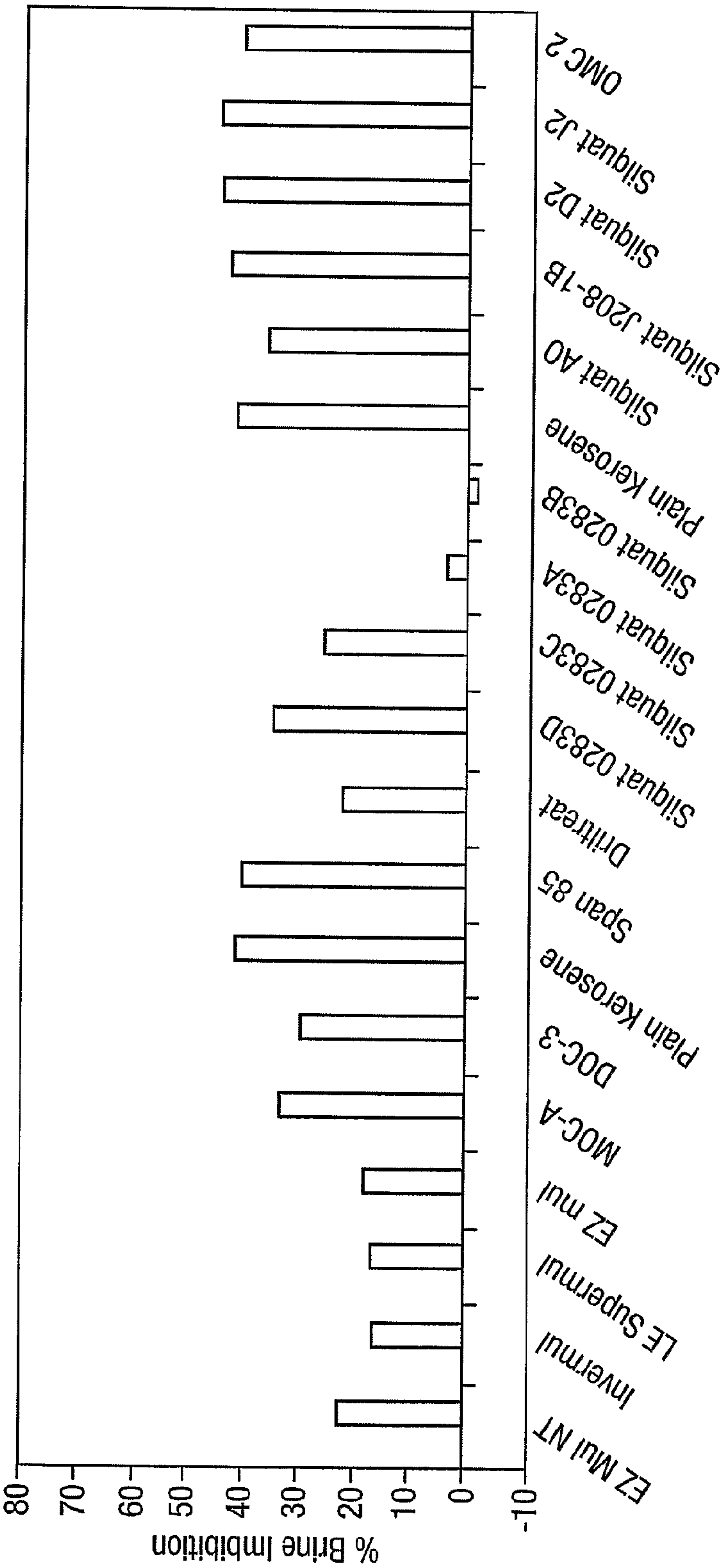
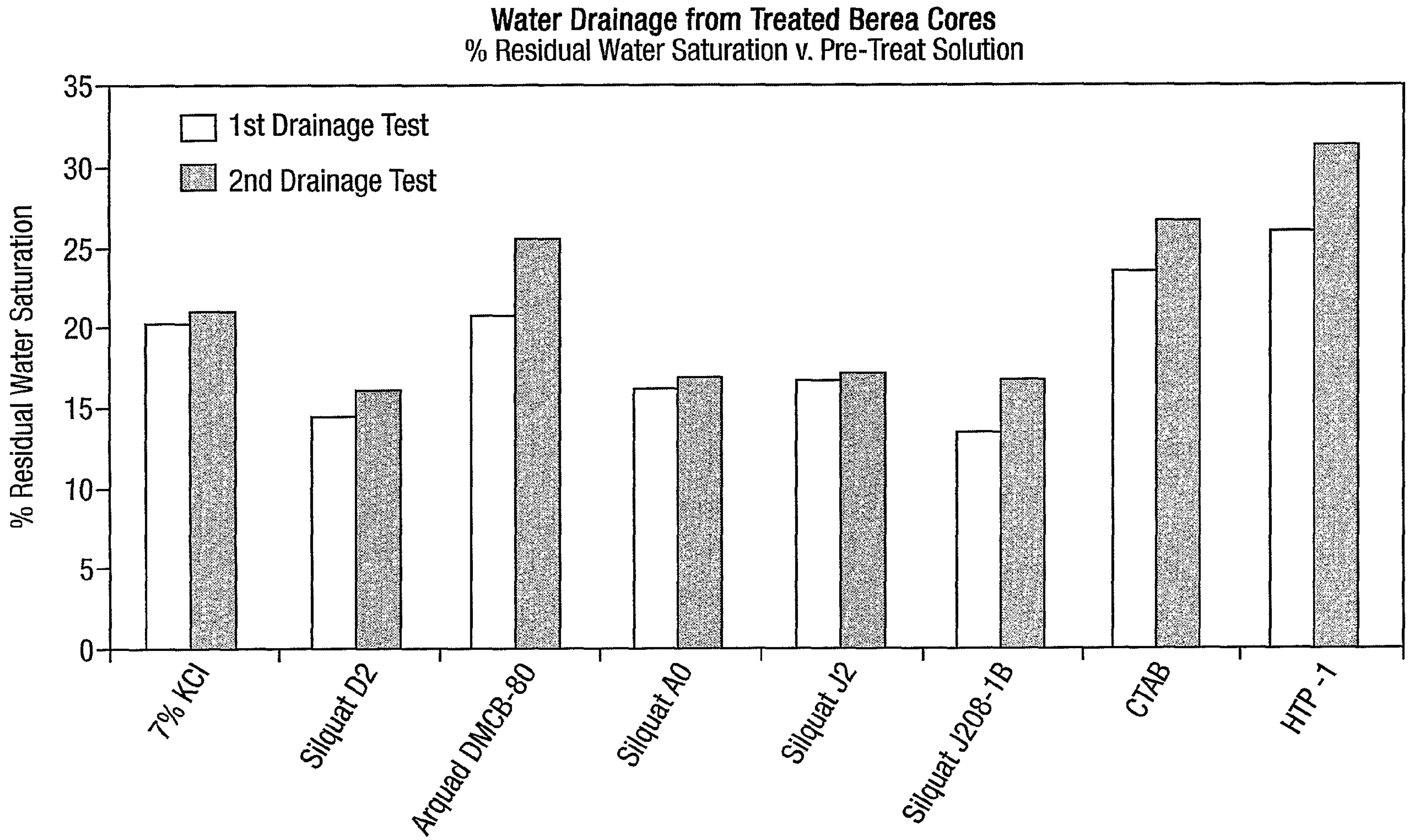


Fig.2.



Water Drainage from Treated Berea Cores
% Residual Water Saturation v. Pre-Treat Solution

Fig.3.

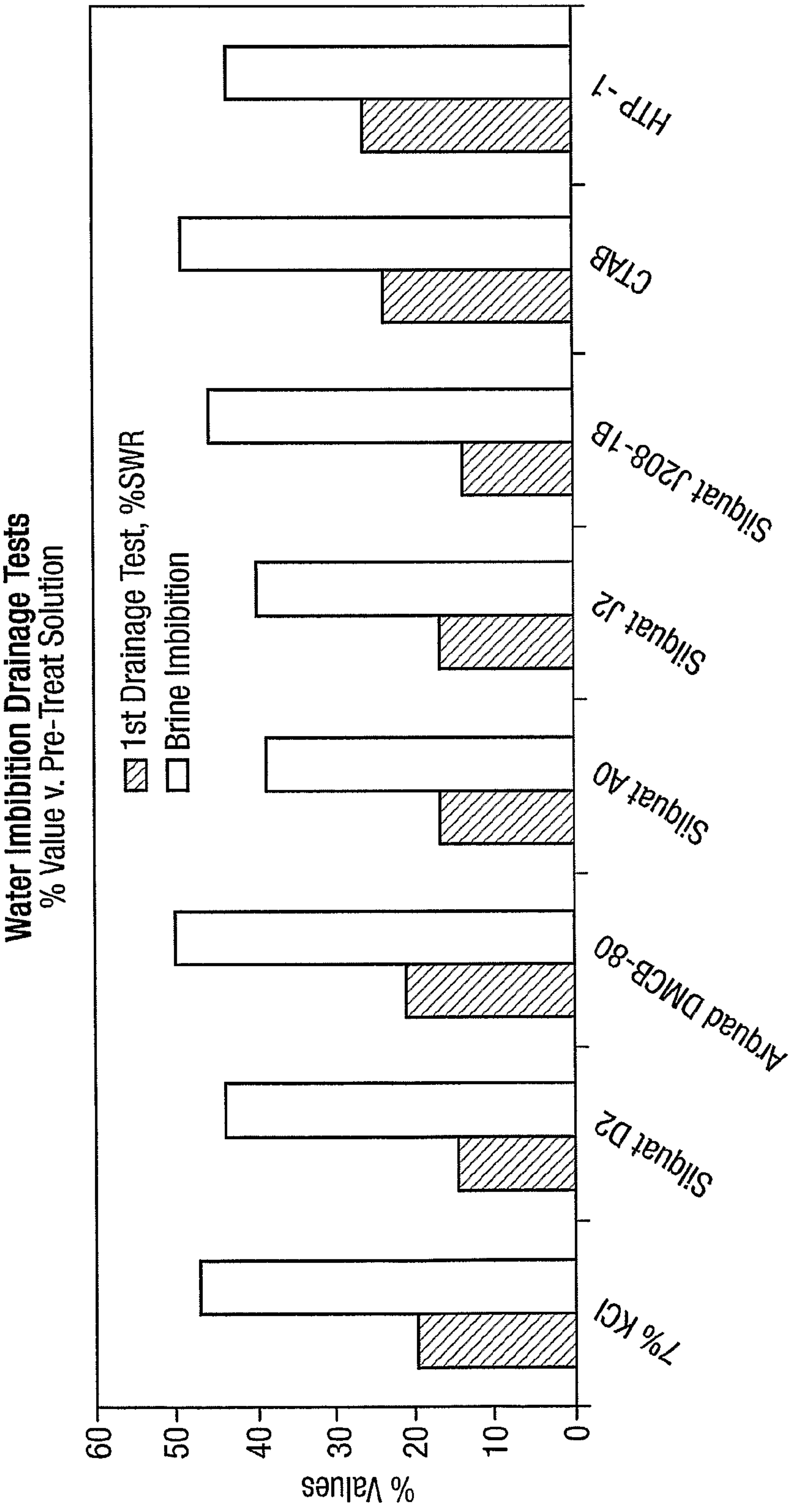

Water Imbibition Drainage Tests
% Value v. Pre-Treat Solution
▨ 1st Drainage Test, %SWR
☐ Brine Imbibition
% Values
0
10
20
30
40
50
60
7% KCl
Silquat D2
Arquad DMCB-80
Silquat A0
Silquat J2
Silquat J208-1B
CTAB
HTP-1

Fig.4.

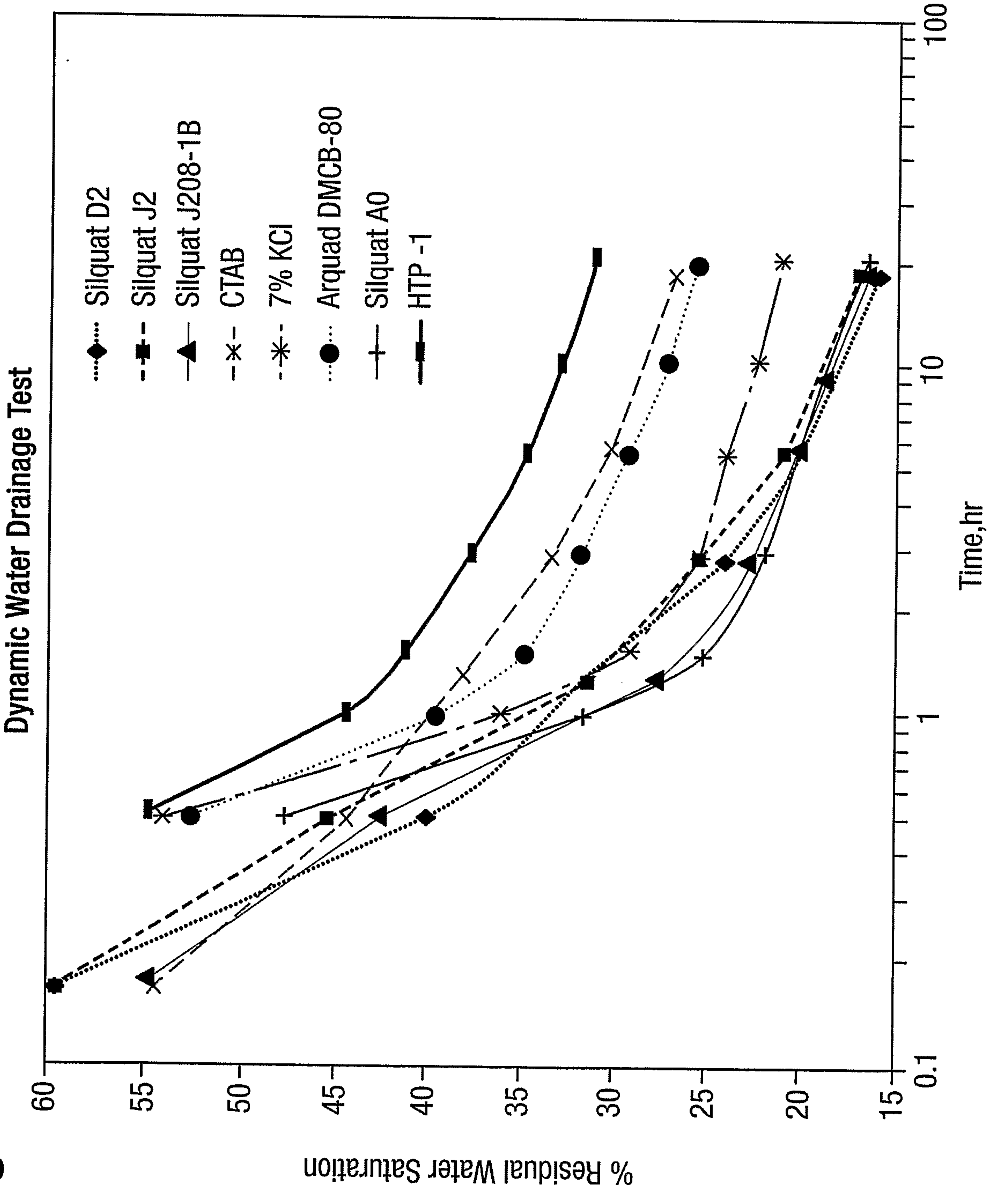

Dynamic Water Drainage Test
Silquat D2
Silquat J2
Silquat J208-1B
CTAB
7% KCl
Arquad DMCB-80
Silquat A0
HTP -1
% Residual Water Saturation
60
55
50
45
40
35
30
25
20
15
0.1
1
10
100
Time,hr

Fig.5.

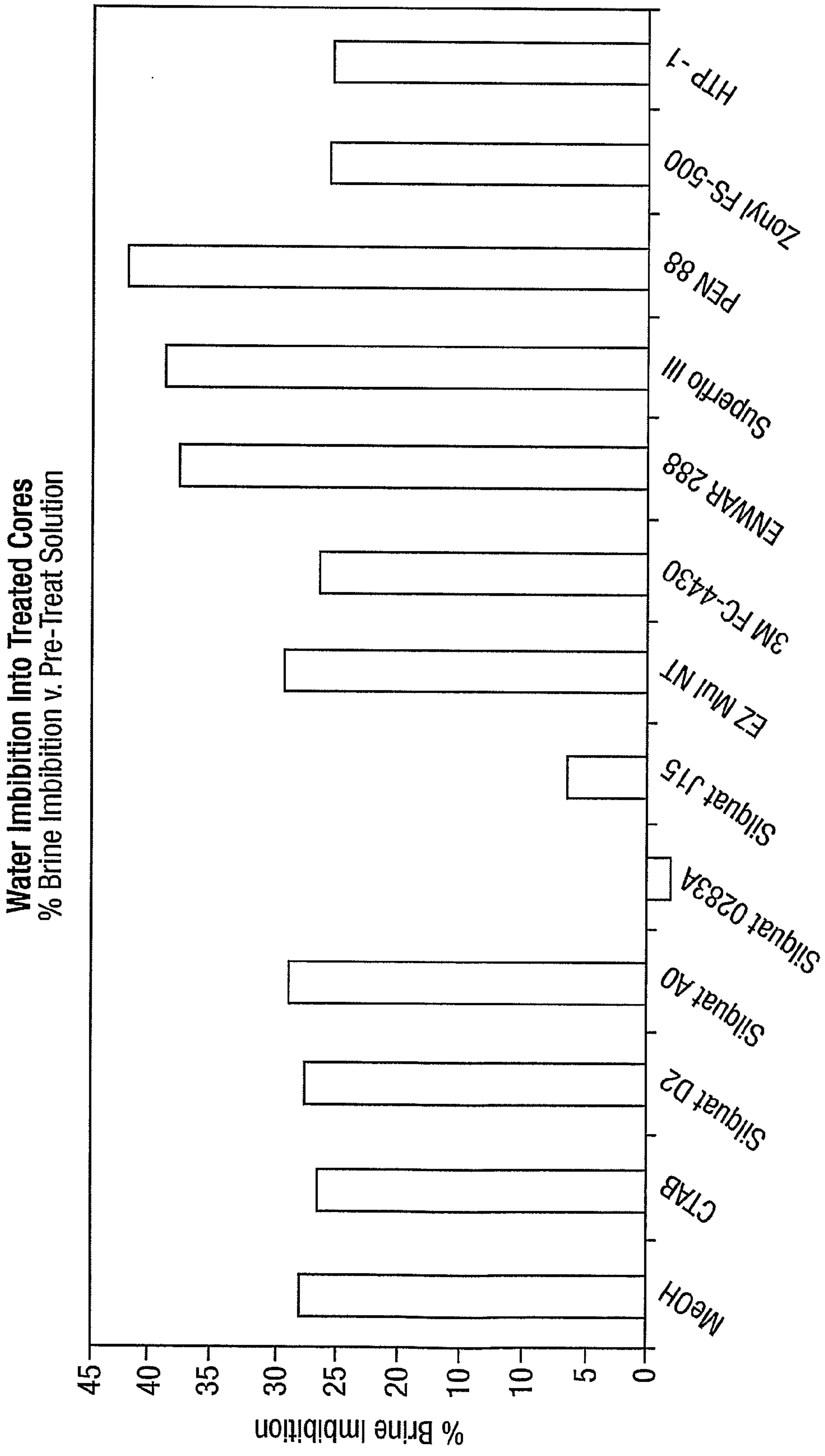

Water Imbibition Into Treated Cores
% Brine Imbibition v. Pre-Treat Solution
% Brine Imbibition
45
40
35
30
25
20
10
10
5
0
HTP-1
Zonyl FS-500
PEN 88
Superflo III
ENWAR 288
3M FC-4430
EZ Mul NT
Silquat J15
Silquat 0283A
Silquat AO
Silquat D2
CTAB
MeOH

Fig.6.

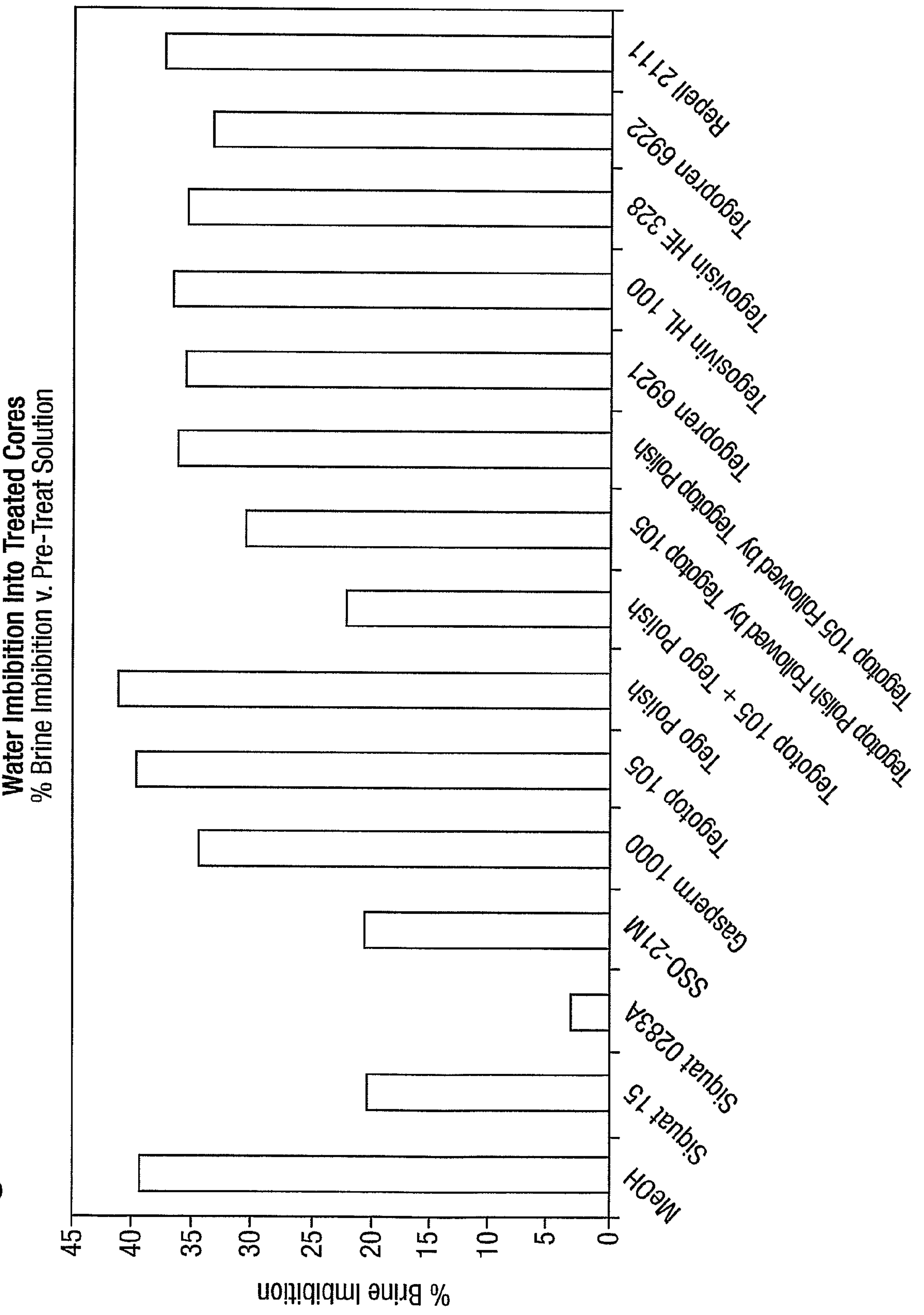
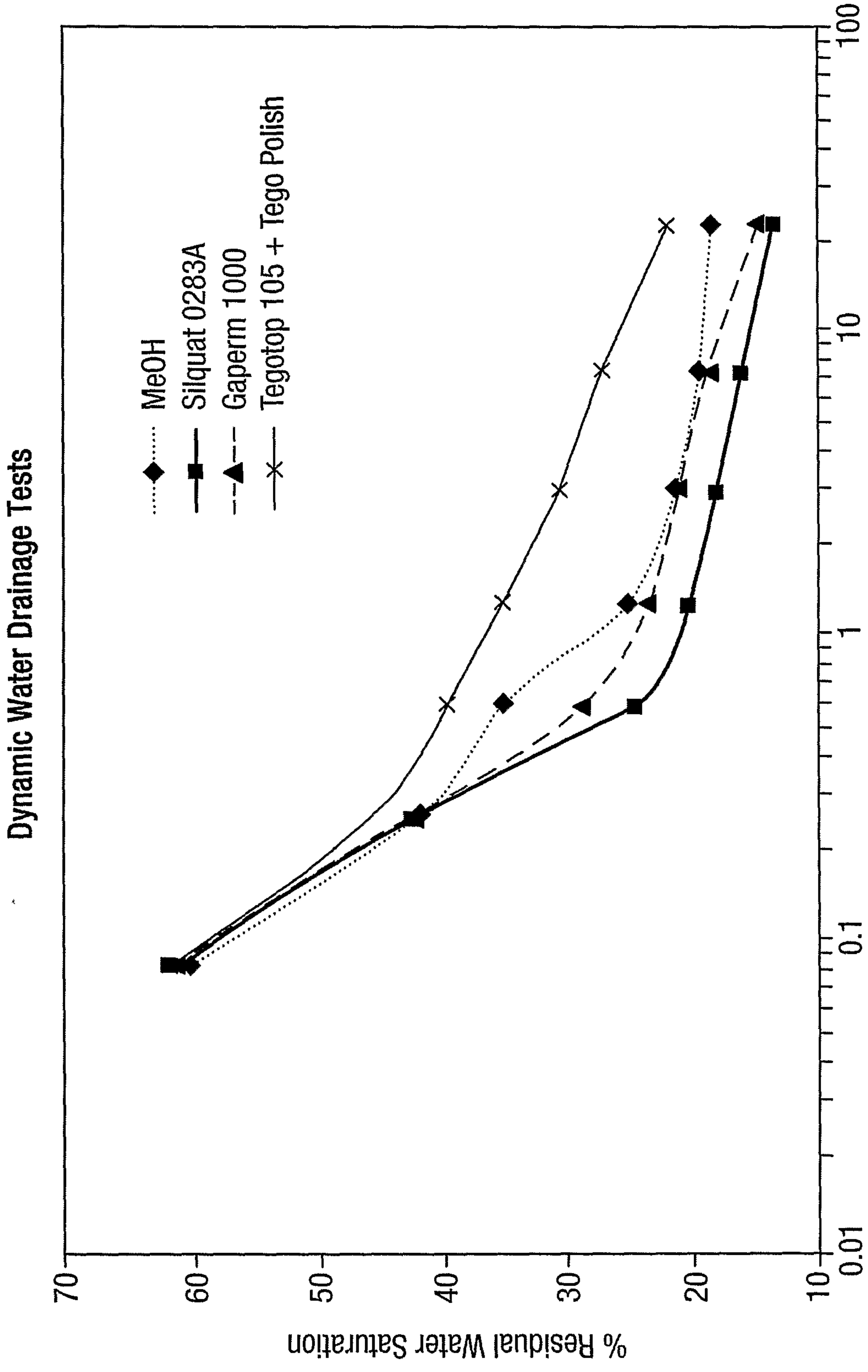

Water Imbibition Into Treated Cores
% Brine Imbibition v. Pre-Treat Solution
% Brine Imbibition
0
5
10
15
20
25
30
35
40
45
MeOH
Siquat 15
Siquat 0283A
SSO-21M
Gasperm 1000
Tegotop 105
Tego Polish
Tegotop 105 + Tego Polish
Tegotop Polish Followed by Tegotop 105
Tegotop 105 Followed by Tegotop Polish
Tegopren 6921
Tegosivin HL 100
Tegovisin HE 328
Tegopren 6922
Repell 2111

Fig.7.


Dynamic Water Drainage Tests
MeOH
Silquat 0283A
Gaperm 1000
Tegotop 105 + Tego Polish
% Residual Water Saturation
70
60
50
40
30
20
10
0.01
0.1
1
10
100