Abstract:

An aqueous slurry composition for use in industries such as the petroleum and pipeline industries includes a particular, an aqueous liquid and a chemical compound that renders the particulate surface extremely hydrophobic. The slurry is produced by rendering the surface of the particulate extremely hydrophobic during or before making the slurry.
Slurry Compositions and the Methods for Making Same

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to an aqueous slurry composition and to a method of making such a composition.

Discussion of the Prior Art

Aqueous particulate slurries are commonly used or encountered in many industries including the petroleum, pipeline, construction and cleaning industries. Slurries are mixtures normally comprising particulates and an aqueous medium and play an essential role in many industrial operations. For example, slurries are used for transporting particulates from one location to another at different distances either above ground, or from the surface to a subterranean formation or from a subterranean formation to the surface. The most commonly used particulates include sand, ceramic particulates, carbonate particulates, glass spheres, bauxite (aluminum oxide) particulates, resin coated particulates and coal particulates. The particulate sizes normally range from about 10 to about 100 US mesh, and the particulate densities are significantly higher than the density of water. For example, the density of sand is at about 2.6 g/cm³ while the density of water is 1 g/cm³. Sand is by far the most commonly used particulate.

To make relatively stable slurry, particulates must be suspended in a liquid medium for a lengthy period at static or/and dynamic conditions. Convention wisdom tells us that the viscosity or viscoelasticity of the liquid medium must be sufficiently high to be able to suspend particulates. The most commonly used
method for increasing viscosity or viscoelasticity of an aqueous liquid is by adding a viscosifier, for example, a natural or synthetic polymer or a viscoelastic surfactant to the liquid medium. It is not unusual that a polymer is used with a foaming agent in order to take advantage of both viscoelastic and foaming properties. However, the use of polymers in slurries increases cost and results in operational difficulties. In particular applications, for example, hydraulic fracturing of subterranean formations, the use of polymers in slurry impedes oil and gas production due to large amounts of residue left in the formation. As for viscoelastic surfactants, although they have fewer residues compared to normal polymers, their cost is usually much higher. In many other applications such as gravel-pack, well completion and sand transportation through pipelines, it is highly desirable to make stable particulate slurry without using a viscosifier.

Hydraulic fracturing operations are used extensively in the petroleum industry to enhance oil and gas production. In hydraulic fracturing, a fracturing fluid is injected through a wellbore into a subterranean formation at a pressure sufficient to initiate fractures, which increase oil and gas production. Frequently, particulates, called proppants, are suspended in the fracturing fluid and transported into fractures as slurry. Proppants include sands, ceramic particulates, bauxite particulates, resin coated sands and other particulates known in the industry. Among them sand is by far the most commonly used proppant.

Fracturing fluids in common use include water-based as well as hydrocarbon-based fluids. In water-based fracturing fluids, a polymer or
viscoelastic surfactant is normally employed to increase the viscoelasticity of the fluid. In most cases the viscoelastic property of the fluids is essential for transporting proppants deep into a formation. At the last stage of the fracturing treatment, fracturing fluid flows back to the surface and the proppants are left in the fracture forming a proppant pack to prevent the fracture from closing after pressure is released. A proppant-filled fracture provides a highly conductive channel that allows oil and/or gas to seep through more efficiently to the wellbore. The conductivity of the proppant pack plays a dominant role in production enhancement. Polymer residues from fracturing fluids are known to greatly reduce the conductivity of the proppant pack.

Compared to polymeric viscosifiers, viscoelastic surfactants cause less damage to formations and proppant packs. However, they are much more expensive.

Accordingly, a need exists for a composition for efficiently transporting proppants deep into a formation at low cost while at the same time causing little damage to the formation and proppant pack. Grain size, concentration, shape and the packing pattern of proppants are also important factors in determining the conductivity. Despite extensive research in recent years, limited progress has been achieved to maximize the conductivity of a proppant pack in a fracture. Therefore, a need exists for making a composition for use in a proppant pack with improved conductivity.

Proppant flowback after fracturing treatments has long been plaguing the petroleum industry. Flowback reduces the amount of proppants in the formation
leading to a less conductive fracture. As disclosed, for example in US Patent 6,047,772, various methods have been tried to solve the flowback problem. In one method, resins are used to coat the proppant and make them very tacky. In doing so, the proppant grains tend to stick together reducing flowback. This method is not only expensive, but the tacky resins introduced in the proppant pack tend to reduce its conductivity. Therefore, there is a need for a composition and method for making slurry, which can form a stable proppant pack resisting proppant flowback, while at the same time has a high conductivity.

When drilling subterranean formations for oil and gas, aqueous-based drilling fluids are normally used. During drilling large amounts of particles, called cuttings are generated. Cuttings have different sizes ranging from fines to pebbles. The drilling fluid is circulated through the wellbore to make slurry with the cuttings in situ and transports them out of wellbore. In most cases, polymers as well as clays are added to the drilling fluids to increase their viscosity/viscoelasticity in order to transport the cuttings efficiently. However, polymers as well as clay fines, can easily penetrate into pores or thin fractures in a formation and reduce formation permeability significantly, especially near wellbore. Reduced formation permeability impedes oil and/or gas production. Therefore it is highly desirable to provide a drilling fluid that can make stable slurry in situ with the cuttings and transport them out of the wellbore, while causing little formation damage.

The escalating price of oil and its alarming depletion rate have caused people to consider using coal as an oil substitute. Several factors have slowed
the substitution of coal for oil. One factor is the difficulty in transporting coal cost-effectively over long distance through pipelines. It is therefore highly desirable to provide a composition for making coal slurry which is stable, highly fluid and cost-effective to transport.

In oil sand operation massive amount of sands are left after oil is stripped from the sand surface. Finding a more cost effective way to transport sands efficiently over distance through pipelines has long been required in the industry. Thus, a composition and a method for making stable and highly fluid sand slurries at low cost would be quite useful.

SUMMARY OF THE INVENTION

Accordingly, one aspect of the present invention relates to an aqueous slurry compositions, which can be used to form a stable, highly conductive proppant pack, for efficiently transporting proppants into a subterranean formation, and for use in transporting drilling cuttings, coal particulates and sands.

The invention also relates to an aqueous slurry composition comprising particulates, an aqueous liquid and a chemical compound that renders the surface of the particulates extremely hydrophobic, and the method of making such slurry composition.

The invention still further relates to a slurry composition comprising particulates, an aqueous liquid, a chemical compound that renders the surface of the particulates extremely hydrophobic and a gas, and the method of making such slurry composition.
The invention also relates to a slurry composition comprising particulates, an aqueous liquid, a chemical compound that renders the surface of the particulates extremely hydrophobic and a surfactant.

The invention also relates to a slurry composition comprising particulates, an aqueous liquid, a chemical compound that renders the surface of the particulates extremely hydrophobic, a surfactant and a gas, and the method of making such slurry composition. The invention also relates to a method of making an aqueous slurry composition comprising steps of first rendering the particulate surface extremely hydrophobic and then mixing the treated particulates with an aqueous liquid, or an aqueous liquid containing a gas.

The invention in another aspect also relates to methods of making the aqueous slurry compositions, including for various applications including hydraulic fracturing, drilling, gravel-pack, transportation through pipelines, blasting and tunneling.

DETAILED DESCRIPTION OF THE INVENTION

It is discovered in the present invention that when the surface of particulates according to the invention become extremely hydrophobic, a slurry made with such particulates has several novel properties. For example, particulates tend to move cohesively instead as individual grains; the bulk volume of settled particulates tend to be significantly greater than in a slurry formed by convention methods under the same conditions; the particulate pack formed tends to have high conductivity and can be easily dewatered, and the slurry tends to be fluid and stable at static or dynamic conditions without using a
viscosifier. The larger bulk volume of the particulate pack indicates a larger porosity and therefore higher conductivity. This is particularly beneficial for improving fracturing treatment, since, as mentioned above, the conductivity of the proppant pack is the dominant property affecting fracturing treatments. The extremely hydrophobic surface of the particulate further reduces the dragging force exerted by the fluid and makes it more difficult for proppants to be carried away by the fluid once the particulates become completely settled. This is particularly beneficial for minimizing proppant flowback after fracturing treatments, leading to increased proppant conductivity. In conventional slurries, viscosity or viscoelasticity of the liquid plays a dominant role while the interfacial interactions between the particulate surface and the liquid play negligible role. However, it is discovered in the present invention that when the surface of the particulate becomes extremely hydrophobic, the interfacial interactions between the surface and the liquid become increasingly important.

In general, the interfacial interactions between a solid substrate and a liquid mainly depend on the surface properties of the solid and the surface tension of the liquid. Normally the macroscopic properties of a solid surface can be characterized by observing the shape of a liquid droplet on the solid substrate, which is the result of free energy of the surface, as well as the free energy of the liquid. When a liquid does not completely wet a surface, it forms an angle $\theta$, which is known as the contact angle. The contact angle is the angle formed between a solid substrate and the tangent line at the point of contact between a liquid droplet and the solid substrate. The contact angle can be measured directly
on macroscopic, smooth, nonporous, planar solid substrates by merely placing a
droplet of the liquid or solution on the solid substrate and determining the contact
angle by any of number of techniques. The values of contact angles between
many solids and aqueous liquid are provided in various books and scientific
publications, which will be known to those skilled in the art. It is known that the
majority of naturally occurring minerals are hydrophilic. It is also known that
certain hydrocarbon compounds, for example, some conventional quaternary
surfactants, amine surfactants and cationic polyacrylamides can be used to
reduce the surface energy of certain particulates and make the particulate
surface less hydrophilic or more hydrophobic. However, the "hydrophobicity"
impacted by such compounds is not high enough to be included in the term of
"extremely hydrophobic" as in the case of the present invention. In the present
invention, "extremely hydrophobic" means that the contact angle of water on the
solid substrate is greater than about 90°. At such high contact angles, water does
not wet the surface of the solid and instead contracts on the solid surface and
forms beads. The chemical compounds that can render a particulate surface
extremely hydrophobic are referred as "extremely hydrophobic rendering
compounds" (EHRC) for the sake of simplicity. EHRC normally are those
compounds that contain organosilane or organosiloxane groups. Because of
such groups, EHRC are able to impart hydrophobicity to solid surface to a level
that conventional hydrocarbon surfactants or polymers are not able to achieve.
These compounds are known to render many inorganic solid surfaces extremely
hydrophobic.
Slurries according to the invention can be made on the ground or in situ in a subterranean formation. Such slurries have numerous applications in many industries, including for (a) transporting particulates over various distances, either on the surface of the ground, from the surface to a subterranean formation or from a subterranean formation to the surface, and (b) well service operations including stimulation, drilling, completion, gravel-pack, controlling sand production and the like.

Furthermore, a gas can be mixed into the slurries of the invention. Suitable gases for use in the slurry include air, carbon dioxide, nitrogen, methane and mixtures thereof. The gas can be introduced into the slurries during preparation thereof. For example, when the slurry is pumped through a pipe, gas such as nitrogen can be introduced into the slurry, or gas such as air can be simply mixed into the slurry through a sufficient rate of agitation.

In the present invention, "aqueous liquids" means water, salt solutions, water containing an alcohol or other organic solvents. It should be understood that the additives other than water in the aqueous liquid are used in amounts or in a manner that does not adversely affect the present invention. One can also add polymers into the aqueous liquid. For example, in so-called slick-water fracturing operations, a small amount of polymer is normally added into an aqueous liquid to reduce friction pressure during pumping.

The size of particulates in compositions according to the invention is about 10-100 US mesh, which is about 150 to 1400 µm. It should be understood that the size distribution of particulates can be narrow or wide. Suitable particulates
include sands, ceramic particulates, glass beads, bauxite particulates, resin coated sands, carbonates and coal particulates.

It is known that many organosilicon compounds including organosiloxane, organosilane, fluoro-organosiloxane and fluoro-organosilane compounds are commonly used to render various surfaces extremely hydrophobic. For example, see United States patent nos. 4,537,595; 5,240,760; 5,798,144; 6,323,268; 6,403,163; 6,524,597 and 6,830,811. It is normally not difficult for those skilled in the art to find suitable organosilicon compounds to render a solid surface extremely hydrophobic. However, it discovered in the present invention that when the surfaces of particulates are rendered extremely hydrophobic in aqueous slurry, the slurry exhibits novel properties which are not seen in conventional aqueous slurry. For example, particulates tend to move cohesively instead as individual grains; the bulk volume of settled particulates tend to be significantly greater than in a slurry formed by convention methods under the same conditions; the particulate pack formed tends to have high conductivity and be easily dewatered, and the slurry tends to be fluid and stable at static or dynamic conditions without using a viscosifier.

Organosilanes are compounds containing silicon to carbon bonds. Organosiloxanes are compounds containing Si-O-Si bonds. Polysiloxanes are compounds in which the elements silicon and oxygen alternate in the molecular skeleton, i.e., Si-O-Si bonds are repeated. The simplest polysiloxanes are polydimethylsiloxanes. Polysiloxane compounds can be modified by various organic substitutes having different numbers of carbons, which may contain N, S,
or P moieties that impart desired characteristics. For example, cationic polysiloxanes are compounds in which one or two organic cationic groups are attached to the polysiloxane chain, either at the middle or the end. Normally the organic cationic group contains at least 10 carbons and may contain a hydroxyl group or other functional groups containing N or O. The most common organic cationic groups are alkyl amine derivatives including secondary, tertiary and quaternary amines (for example, quaternary polysiloxanes including, quaternary polysiloxanes including mono- as well as di-quaternary polysiloxanes, amido quaternary polysiloxanes, imidazoline quaternary polysiloxanes and carboxy quaternary polysiloxanes.

Similarly, the polysiloxane can be modified by organic amphoteric groups, where one or two organic amphoteric groups are attached to the polysiloxane chain, either at the middle or the end, and include betaine polysiloxanes and phosphobetaine polysiloxanes.

Similarly, the polysiloxane can be modified by organic anionic groups, where one or two organic anionic groups are attached to the polysiloxane chain, either at the middle or the end, including sulfate polysiloxanes, phosphate polysiloxanes, carboxylate polysiloxanes, sulfonate polysiloxanes, thiosulfate polysiloxanes. The organosiloxane compounds also include alkylsiloxanes including hexamethyldichlorosiloxane, octamethyldichlorotetrasiloxane, decamethyldichloropentasiloxane, hexamethyldisiloxane, hexaethyldisiloxane, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane. The organosilane compounds include
alkylchlorosilane, for example methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, octadecyltrichlorosilane; alkyl-alkoxysilane compounds, for example methyl-, propyl-, isobutyl- and octyltrialkoxysilanes, and fluoro-organosilane compounds, for example, 2-(n-perfluoro-octyl)-ethyltriethoxysilane, and perfluoro-octyldimethyl chlorosilane.

Other types of chemical compounds, which are not organosilicon compounds, which can be used to render particulate surface extremely hydrophobic are certain fluoro-substituted compounds, for example certain fluoro-organic compounds.

Further information regarding organosilicon compounds can be found in Silicone Surfactants (Randal M. Hill, 1999) and the references therein, and in United States Patent Nos. 4,046,795; 4,537,595; 4,564,456; 4,689,085; 4,960,845; 5,098,979; 5,149,765; 5,209,775; 5,240,760; 5,256,805; 5,359,104; 6,132,638 and 6,830,811 and Canadian Patent No. 2,213,168.

Organosilanes can be represented by the formula

$$R_nSiX(4-n)$$

wherein R is an organic radical having 1-50 carbon atoms that may posses functionality containing N, S, or P moieties that imparts desired characteristics, X is a halogen, alkoxy, acyloxy or amine and n has a value of 0-3. Examples of suitable organosilanes include:

- $\text{CH}_3\text{SiCl}_3$, $\text{CH}_3\text{CH}_2\text{SiCl}_3$, $(\text{CH}_3)_2\text{SiCl}_2$, $(\text{CH}_3\text{CH}_2)_2\text{SiCl}_2$, $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$,
- $(\text{C}_6\text{H}_5)\text{SiCl}_3$, $(\text{CH}_3)_3\text{SiCl}$, $\text{CH}_3\text{HSiCl}_2$, $(\text{CH}_3)_2\text{HSiCl}$, $\text{CH}_3\text{SiBr}_3$, $\text{CH}_3\text{SiCl}_3$.
(C₆H₅)SiBr₃, (CH₃)₂SiBr₂, (CH₃CH₂)₂SiBr₂, (C₆H₅)₂SiBr₂, (CH₃)₃SiBr, CH₃HSiBr₂,
(CH₃)₂HSiBr, Si(OCH₃)₄, CH₃Si(OCH₃)₃, CH₃Si(OCH₂CH₃)₃,
CH₃Si(OCH₂CH₂CH₃)₃, CH₃Si[O(CH₂)₃CH₃]₃, CH₃CH₂Si(OCH₂CH₃)₃,
C₆H₅Si(OCH₃)₅, C₆H₅CH₂Si(OCH₃)₃, C₆H₅Si(OCH₂CH₃)₃, CH₂=CHCH₂Si(OCH₃)₃,
(CH₃)₂Si(OCH₃)₂, (CH₂=CH)Si(CH₃)₂Cl, (CH₃)₂Si(OCH₂CH₃)₂,
(CH₃)₂Si(OCH₂CH₂CH₃)₂, (CH₃)₂Si(OCH₃)₂, (CH₃CH₂)₂Si(OCH₂CH₃)₂,
(C₆H₅)₂Si(OCH₃)₂, (C₆H₅CH₂)₂Si(OCH₃)₂, (C₆H₅)₂Si(OCH₂CH₃)₂,
(CH₂=CH₂)₂Si(OCH₃)₂, (CH₂=CHCH₂)₂Si(OCH₃)₂, (CH₃)₃SiOCH₃, CH₃HSi(OCH₃)₂,
(CH₃)₃Si(OCH₂CH₂CH₃)₃, CH₂=CHCH₂Si(OCH₂CH₂OCH₃)₂,
(C₆H₅)₂Si(OCH₂CH₂OCH₃)₂, (CH₃)₂Si(OCH₂CH₂OCH₃)₂,
(CH₂=CH₂)₂Si(OCH₂CH₂OCH₃)₂, (CH₂=CHCH₂)₂Si(OCH₂CH₂OCH₃)₂,
(C₆H₅)₂Si(OCH₂CH₂OCH₃)₂, CH₃Si(CH₃COO)₃, 3-aminotriethoxysilane,
methyltriethylchlorosilane, butyltrichlorosilane, diphenyldichlorosilane,
vinyldichlorosilane, methyltrimethoxysilane, vinyltriethoxysilane,
vinyldiisopropylmethoxysilane, methacryloxypropyltrimethoxysilane,
glycidoxypropyltrimethoxysilane, aminopropyltriethoxysilane, divinylidi-2-
methoxysilane, ethyltributoxysilane, isobutyltrimethoxysilane,
hexyltrimethoxysilane, n-octyltriethoxysilane, dihexylmethoxysilane,
Octadecyltrimethoxysilane, octadecyltrichlorosilane,
Octadecyltrimethylchlorosilane, octadecyltrimethylmethoxysilane and quaternary
ammonium silanes including 3-(trimethoxysilyl)propyltrimethoxysilane,
chineammonium chloride, 3-(trimethoxysilyl)propyltrimethoxysilane ammonium bromide, 3-(trimethoxysilyl)propyltrimethoxysilane didecylmethyl ammonium chloride,
Among different organosiloxane compounds which are useful for the present invention, polysiloxanes modified with organic amphoteric or cationic groups including organic betaine polysiloxanes and organic quaternary polysiloxanes are examples. One type of betaine polysiloxane or quaternary polysiloxane is represented by the formula

$$\text{(II)}$$

wherein each of the groups $R_i$ to $R_6$, and $R_8$ to $R_{10}$ represents an alkyl containing 1-6 carbon atoms, typically a methyl group, $R_7$ represents an organic betaine group for betaine polysiloxane, or an organic quaternary group for quaternary polysiloxane, and have different numbers of carbon atoms, and may contain a hydroxyl group or other functional groups containing $N$, $P$ or $S$, and $m$ and $n$ are from 1 to 200. For example, one type of quaternary polysiloxanes is when $R_7$ is represented by the group

$$\text{(CH}_3\text{O})_3\text{Si(CH}_2\text{)}_3\text{N}^+\text{(CH}_3\text{)}_2\text{C}_1\text{8}_3\text{H}_3\text{7}_3\text{Cr}.$$
wherein $R_1$, $R_2$, $R_3$ are alkyl groups with 1 to 22 carbon atoms or alkenyl groups with 2 to 22 carbon atoms. $R_4$, $R_6$, $R_7$ are alkyl groups with 1 to 22 carbon atoms or alkenyl groups with 2 to 22 carbon atoms; $R_6$ is $-O-$ or the $NR_8$ group, $R_8$ being an alkyl or hydroxyalkyl group with 1 to 4 carbon atoms or a hydrogen group; $Z$ is a bivalent hydrocarbon group with at least 4 carbon atoms, which may have a hydroxyl group and may be interrupted by an oxygen atom, an amino group or an amide group; $x$ is 2 to 4; The $R_1$, $R_2$, $R_3$, $R_4$, $R_5$, $R_7$ may be the same or the different, and $X^-$ is an inorganic or organic anion including $\text{Cl}^-$ and $\text{CH}_3\text{COO}^-$. Examples of organic quaternary groups include $[\text{R-N}^+(\text{CH}_3)_2^-$

$\text{CH}_2\text{OHCH}_2\text{O-}(\text{CH}_2)_3-] \ (\text{CH}_3\text{COO}^-)$, wherein $R$ is an alkyl group containing from 1-22 carbons or an benzyl radical and $\text{CH}_3\text{COO}^-$ an anion. Examples of organic betaine include $-((\text{CH}_2)_3-O-\text{CH}_2\text{OH})\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$. Such compounds are commercial available. Betaine polysiloxane copolyol is one of examples. It should be understood that cationic polysiloxanes include compounds represented by formula (II), wherein $R_7$ represents other organic amine derivatives including organic primary, secondary and tertiary amines.

Other example of organo-modified polysiloxanes include di-betaine polysiloxanes and di-quatemary polysiloxanes, which can be represented by the formula
wherein the groups $R_{12}$ to $R_{7}$ each represents an alkyl containing 1-6 carbon atoms, typically a methyl group, both $R_{11}$ and $R_{1}$ group represent an organic betaine group for di-betaine polysiloxanes or an organic quaternary group for di-quaternary, and have different numbers of carbon atoms and may contain a hydroxyl group or other functional groups containing $N$, $P$ or $S$, and $m$ is from 1 to 200. For example, one type of di-quaternary polysiloxanes is when $R_{1}$ and $R_{18}$ are represented by the group

\[
\begin{align*}
&\begin{array}{c}
\text{R}^1 \\
\text{Z} \\
\text{R}^3
\end{array} - \text{N}^+ - \begin{array}{c}
\text{R}^2 \\
\text{X}^- \\
\text{R}^4
\end{array} \\
&\text{or} \\
&\begin{array}{c}
\text{R}^1 \\
\text{Z} \\
\text{R}^3
\end{array} - \text{N}^+ - \begin{array}{c}
(\text{CH}_2)_x \text{R}^6 \\
\text{CR}^7
\end{array} - \begin{array}{c}
\text{X}^-
\end{array}
\end{align*}
\]

wherein $R^1$, $R^2$, $R^3$, $R^4$, $R^6$, $R^7$, $Z$, $X^-$ and $x$ are the same as defined above.

Such compounds are commercially available. Quaternium 80 (INCI) is one of the commercial examples.

It should be appreciated by those skilled in the art that cationic polysiloxanes include compounds represented by formula (III), wherein $R_{1}$ and $R_{18}$ represents other organic amine derivatives including organic primary, secondary and tertiary amines. It should be apparent to those skilled in the art that there are different mono- and di-quaternary polysiloxanes, mono- and di-betaine polysiloxanes and other organo-modified polysiloxane compounds which
can be used to render the solid surfaces extremely hydrophobic and are useful in the present invention. These compounds are widely used in personal care and other products, for example as discussed in United States patent nos. 4,054,161; 4,654,161; 4,891,166; 4,898,957; 4,933,327; 5,166,297; 5,235,082; 5,306,434; 5,474,835; 5,616,758; 5,798,144; 6,277,361; 6,482,969; 6,323,268 and 6,696,052.

Another example of organosilicon compounds which can be used in the composition of the present invention are fluoro-organosilane or fluoro-organosiloxane compounds in which at least part of the organic radicals in the silane or siloxane compounds are fluorinated. Suitable examples are fluorinated chlorosilanes or fluorinated alkoxy silanes including 2-(n-perfluoro-octyl)ethyltrioxsilane, perfluoro-octy dimethylchlorosilane, (CF₃CH₂CH₂)₂Si(OCH₃)₂, CF₃CH₂CH₂Si(OCH₃)₃, (CF₃CH₂CH₂)₂Si(OCH₂CH₂OCH₃)₂ and CF₃CH₂CH₂Si(OCH₂CH₂OCH₃)₃ and (CH₃O)₃Si(CH₂)₃N⁺(CH₃)₂(CH₂)₃NHC(O)(CF₂)₆CF₃Cr. Other compounds which can be used, but less preferable, are fluoro-substituted compounds, which are not organic silicon compounds, for example, certain fluoro-organic compounds.

It is understood that the particulate surfaces can be hydrophobized either by forming covalent bonds between the particulate surfaces and an EHRC or by adsorption of an EHRC on the particulate surfaces. For example, it is known that chlorosilanes and alkoxy silanes, which usually undergo hydrolysis in aqueous medium under suitable conditions, are used to modify surface through forming covalent bonds. Following hydrolysis, reactive silanol groups are formed, which
can condense with other silanol groups, for example, those on the surface of siliceous materials, to form covalent bonds. For example, methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, their alkoxy derivatives can be used to render glass surface extremely hydrophobic through forming covalent bonds with the glass surfaces. It has been observed that polysiloxanes including various organic modified derivatives tend to have little tendency to hydrolysis under normal conditions. It is believed that they modify the surfaces predominantly by adsorption on the solid surfaces. It is common that solid surfaces, especially inorganic solid surfaces, in an aqueous medium possess charges, either negative or positive, which is influenced significantly by the pH of the aqueous medium. Organic substitutes on polysiloxane molecule, especially ionic ones having charges opposite to those on the solid surface, enhance significantly the adsorption of polysiloxanes on the solid surfaces. For example, a cationic polysiloxane can readily adsorb on sand surface in an aqueous liquid with neutral pH, at which the sand surface possesses negative charges. Similarly, an anionic polysiloxane, for example, a sulfonate polysiloxane tend to adsorb to a carbonate surface in an aqueous liquid more easily at neutral pH.

Slurries according to the present invention can be prepared, for example, by mixing an aqueous liquid with particulates and an EHRC, using conventional mixing method with a sufficient amount of shear. Alternatively, the particulates can be first treated by contacting the particulates with a fluid medium containing an EHRC to render the particulate surfaces extremely hydrophobic and then separating the particulates from the medium. The fluid medium can be a liquid or
a gas. The pre-hydrophobized particulates can later be used to make a slurry. In either case, a gas, including air, nitrogen, carbon dioxide, methane and mixtures thereof, can also be mixed into the slurries under agitation. Water is the most preferred aqueous liquid for making the slurry.

It is found in the present invention that adding suitable conventional hydrocarbon surfactants into the slurry composition is also useful. It should be understood that the surfactants should be added to the slurry at concentrations and in a manner which would not adversely affect the slurry. For example, when a surfactant is added to the slurries, one should try to avoid forming insoluble precipitates with the EHRC, or changing greatly the wettability of the particulate surface, or greatly reducing the surface tension of the aqueous liquid. For example, mixing cationic polysiloxane with an anionic hydrocarbon-surfactant, or vice versa, is normally not preferred, due to the tendency of causing undesired precipitations. Instead, when a cationic polysiloxane is used a cationic or an amphoteric hydrocarbon surfactant is more preferred. Similarly, when an anionic polysiloxane is used, an anionic surfactant or an amphoteric hydrocarbon surfactant is more preferred. Principles about surfactant compatibility are known to those skilled in the art. Also a very low surface tension of the aqueous liquid is not desirable. When the surface tension of the liquid is too low, more water can be added or some of the aqueous fluid containing surfactants can be replaced with water.

The slurries can be prepared on surface (above ground) or in a subterranean formation where the particulates, an aqueous fluid, and an EHRC,
for example a di-quaternary polysiloxane, are mixed in situ. Examples of situations where in situ mixing is used include drilling and wellbore cleanout operations. Alternatively, the particulates can be first mixed with a liquid in which an EHRC is dispersed or dissolved and then the particulates separated from the liquid or dried. The thus treated particulates can subsequently be used to make the slurry. Various proppants including sands, ceramic particulates or resin coated sands can be treated according to the present invention during manufacturing process. The thus prepared hydrophobic particulates can be used as proppants in fracturing operations. Depending on the amount and size of the particulates in the slurry, a wide range of EHRC concentration can be used to render the particulate surface extremely hydrophobic. Usually the amount of EHRC added is very small and has no apparent effect on the viscosity of the liquid to which it is added. For example, the concentration of EHRC in the slurry can be as low as a few ppm to hundreds of ppm. In most applications, it is unnecessary to add EHRC in an amount larger than 1 percent of the total liquid.

The following examples serve to illustrate the concepts of the present invention.

Example 1

50 ml of water and 50 grams of 20/40 mesh fracturing sands were added into each of two glass bottles (200ml). 0.5 ml of Tegopren 6923, a di-quaternary polydimethylsiloxane from Degussa Corp., was added into one of the bottles and the other bottle was used as control. The bottles were vigorously shaken and then let stand to allow sands settle down. The volumes of the settled sands in the
two bottles were compared. In the bottle containing Tegopren 6923, the volume of the settled sands was about 40 percent greater than the one without, and the sands are more fluid. When the bottles were tilted slowly, the settled sands in the control tended to move as individual sand grains, while the settled sands containing Tegopren 6923 tended to move as cohesive masses.

Example 2

50 ml water, 50 grams of 20/40 mesh fracturing sands, 0.5 ml of Tegopren 6923 and 0.1 ml of Aquard 18-50, C18-trimethylammonium chloride, a cationic hydrocarbon surfactant from Akzo Nobel Corp., was mixed into a glass bottle (200ml). The bottles were vigorously shaken and then let stand to allow sands settle down. All sands settled down to the bottom immediately in the control bottle. In the bottle containing Tegopren 6923, the sands immediately following agitation were fully distributed in the water making a stable slurry. After one hour, about half amount of sands settled on the bottom while the other half was floating on the top.

Example 3

100 ml of water and 50 grams of 20/40 mesh ceramic proppants were added into each of two glass bottles (200ml). 0.5 ml of TEGO Betaine 810, capryl/capramidopropyl betaine, an amphoteric hydrocarbon surfactant from Degussa Corp., and 1 ml of a solution containing 20% Tegopren 6924, a di-quaternary polydimethylsiloxane from Degussa Corp., and 80% of ethylene glycol mono-butyl ether were added into one of the bottles, and the other bottle was used as control. The bottles were vigorously shaken and then let stand to
allow proppants settle down. All proppants settled down to the bottom immediately in the control bottle. In the one containing Tegopren 6924 about 25% of proppants was floating on the top and the remaining 75% settled on the bottom, while the volume of the 75% settled proppants was still significantly larger than that in the control one. When the bottles were tilted slowly, the settled proppants in the bottle with straight water tended to move as individual grains, while the settled proppants in the one containing Tegopren 6924 tended to move as cohesive masses.

Example 4

100 ml of water and 50 grams of 40/70 mesh fracturing sand were added into each of two glass bottles (200ml). 0.1 ml of Tegopren 6924 and 0.1 ml of TEGO Betaine 810, were added and further added 2 wt% KCl. The other bottle was used as control. The bottles were vigorously shaken and then let stand to allow sands settle down. The volumes of the settled sands in the two bottles were compared. All sands settled down to the bottom immediately in the control bottle. In the bottle containing Tegopren 6924, about 15% of sands was floating on the top and the remaining 85% settled on the bottom, while the volume of the 85% settled sand was still significantly larger than that in the control one. When the bottles were tilted slowly, the settled sands in the bottle with straight water tended to move as individual grains, while the settled sands in the one containing Tegopren 6924 tended to move as cohesive masses.

Example 5
100 ml of water and 50 grams of 40/70 mesh fracturing sand were added into each of two glass bottles (200ml). 0.5 ml of TEGO Betaine 810 and 1 ml of a solution containing 20% Tegopren 6924 and 80% of ethylene glycol mono-butyl ether were added into one of the bottles. After thoroughly mixing the sands were separated from the liquid and dried at room temperature. The pre-hydrophobized sands were mixed with 100ml water and shaken vigorously. All sands settled down to the bottom immediately in the control bottle. In the bottle containing pre-hydrophobized sands, about 40% of sands was floating on the top and the remaining 60% settled on the bottom, while the volume of the 60% settled sand was still significantly larger than that in the control one. When the bottles were tilted slowly, the settled sands in the bottle with straight water tended to move as individual grains, while the settled pre-hydrophobized sands tended to move as cohesive masses.

Example 6

100 ml of water and 50 grams of coal particulates were added into each of two glass bottles (200ml). 0.5 ml of TEGO Betaine 810 and 1 ml of a solution containing 20% Tegopren 6924 and 80% of ethylene glycol mono-butyl ether were added into one of the bottles. The other bottle was used as control. The bottles were vigorously shaken and then let stand to allow coal particulates settle down. The coal particulates in the control bottle settled down immediately. In the bottle containing Tegopren 6924, about 45% of coal particulates was floating on the top and the remaining 55% settled on the bottom, while the volume of the
55% settled coal particulates was about only 15% smaller than the volume of 100% of the coal particles in the control one.

Example 7

100 ml of water and 50 grams of 40/70 mesh fracturing sand were added into each of two glass bottles (200ml). 0.03 ml of Maquat QSX, a quaternary silane compound characterized as triethoxysilyl soyapropyl dimonium chloride in butylene glycol, was added into one of the bottles. The other bottle was used as control. After being thoroughly mixed the liquid above the settled sand in the one containing Maquat QSX was discarded and replaced with same amount of water. The bottles were vigorously shaken and then let stand to allow sands settle down. The volumes of the settled sands in the two bottles were compared. All sands settled down to the bottom immediately in the control bottle. In the bottle containing Maquat QSX, about 5% of sands was floating on the top and remaining 95% settled on the bottom, while the volume of the 95% settled sand was still significantly larger than the control one. When the bottles were tilted slowly, the settled sands in the control bottle tended to move as individual grains, while the settled sands in the one containing Maquat QSX tended to move as cohesive masses.

Example 8

100 ml of water and 50 grams of 20/40 mesh resin coated sands were added into each of two glass bottles (200ml). 1 ml of a solution containing 20% Tegopren 6924 and 80% of ethylene glycol mono-butyl ether were added into one of the bottles, and the other bottle was used as control. The bottles were
vigorously shaken and then let stand to allow resin coated sands settle down. All resin coated sands settled down to the bottom immediately in the control bottle. In the bottle containing Tegopren 6924, about 15% of the resin coated sands was floating on the top and the remaining 85% settled on the bottom, while the volume of the 85% settled sand was still significantly larger than that in the control one. When the bottles were tilted slowly, the settled sands in the bottle with straight water tended to move as individual grains, while the settled sands in the one containing Tegopren 6924 tended to move as cohesive masses.

Example 9

50 gram of 30/50 mesh fracturing sands were mixed with 10 ml of silicone oil (polydimethylsiloxane) of viscosity of 20 cp and left on filter paper at room temperature for 24 hours. 10 gram of the pre-hydrophobized sands and 50 ml of water is mixed into glass bottle (200 ml). 10 gram of untreated sands into 50 ml of water was used as control. The bottles were vigorously shaken and then let stand to allow resin sands settle down. All sands in the control bottle settled down to the bottom immediately. In the bottle containing pre-hydrophobized sands, a small amount of sands was floating on the top of water. The volume of settled pre-treated sands is significant larger than that in the control one. When the bottles were tilted slowly, the settled sands in the control bottle tended to move as individual grains, while the settled pre-hydrophobized sands tended to move as cohesive masses.

Example 10
100 ml of water and 25 grams 30/50 fracturing sands were added into each of two glass bottles (200ml). 0.05 ml of Tegopren 6922, a di-quaternary polydimethylsiloxane from Degussa Corp., was added into one of the bottles. The other bottle was used as control. The bottles were vigorously shaken and then let stand to allow coal particulates settle down. The sands in the control bottle settled down immediately. In the bottle containing Tegopren 6922, sands settled down slower and a layer of sands was floating on the top and furthermore the sands were more fluid than those in the control one. The volume of settled sands in the one containing Tegopren 6922 was about twice of that in the control.

Example 11

A confidential and experimental hydraulic fracturing treatment was carried out in a gas well. The depth of the well was about 2500m and the formation temperature was about 76 °C. The fracturing fluid used was slick water, where a small amount of polymer was added into water to reduce friction pressure. Two proppants were used, one was 40/70 sands and the other was 30/50 sands. During the proppant stage, Tegopren 6922 was added into the fracturing fluid by continuous mixing at concentrations of 1 L/m³ to 3 L/m³ through the proppant stage, where the slurry was prepared and pumped into the formation through wellbore. Nitrogen gas was mixed with the fluid and the slurry during the operation. The samples taken during the operation showed that compared to sands in conventional slick water fracturing, the sands settled down slower and were more fluid.
As mentioned above, the present invention is particularly useful in many applications in the petroleum industry as well as in other industries. Examples include various well service operations including hydraulic fracturing, gravel pack, wellbore cleanout and drilling, particulate transportation through pipeline, sand blasting, and excavation of a geological formation including tunneling, dredging, digging and the like.

When used in a hydraulic fracturing operation, a large amount of proppants can effectively be transported into a subterranean formation without using a viscosifier. It is not only cost-effective but also eliminates damage to the formation and proppant pack caused by polymer residues. An EHRC, for example, a di-quaternary polysiloxane can be mixed with an aqueous liquid and proppants on-the-fly to make the slurry and subsequently pumped into the formation during the proppant stage, either with or without a gas, or furthermore, a hydrocarbon surfactant, for example, a betaine surfactant, can be combined into the composition. It is particularly beneficial to use the slurry in so-called slick-water fracturing treatment. In conventional slick-water fracturing operations, due to the low viscosity of the fluid, only low concentrations of proppants can be effectively pumped deep into a formation, and moreover the proppants tend to settle down on the bottom of the fracture, resulting in lower conductivity. With the composition of the present invention, high concentration of proppants can easily be pumped deep into a formation and the proppants are more evenly distributed in the fracture, leading to improved conductivity of the proppant pack. Other aqueous fracturing fluids including water, brine, cross-linked polymer fluid and
viscoelastic surfactant fluid can also be employed in the present invention. An EHRC can be added straightly or premixed with a solvent or added as an emulsion during an operation. Similarly, one can use pre-hydrophobised proppants to make the slurries in the fracturing operations. Another benefit of the slurries of the present invention is that the aqueous liquid is re-useable after it is separated from the particulates. This has great significance considering there is limited water supply in a number of places.

The present invention also provides a new method for preventing proppant flowback after a fracturing treatment. In field operations, proppants can be pumped into a formation using the composition of the present invention. Alternatively, a fluid medium containing an EHRC can be pumped into the formation following the proppant stage to mix with particulates already in the formation. The particulates in the slurry tend to move cohesively in contrast to conventional slurries under the same conditions. It is worth noting that the cohesiveness among the proppant grains in the present slurry originates from hydrophobic interactions, instead of tackiness as described, for example in US Patent 6,047,772.

The slurry of the present invention is particularly useful in gravel-pack operations where sand slurry is normally pumped into a wellbore to prevent excessive amount of sands from flowing into the wellbore from the formation. The present method is cost effective and the sand pack formed has a high conductivity. Similarly, the slurry can also be used in so-called formation consolidation operations. In such an operation, a fluid containing an EHRC is
injected into a formation to increase cohesiveness among sand grains to consolidate the formation and to reduce sand production.

In drilling operations, an EHRC can be added into a water-based drilling fluid. It is particularly useful when the EHRC is added to water or brine for use as a drilling fluid. During a drilling operation, the fluid forms slurry in situ with cuttings and transports the cuttings out of the wellbore. A gas such as nitrogen or carbon dioxide can be mixed with the slurry during drilling. Since it is not necessary to use polymers or clays to viscosity the fluid, there is much less formation damage. Moreover, the cuttings can be easily removed on the surface and the aqueous liquid becomes re-useable. Different formations including sandstone, carbonate, shale and coal seams can be drilled using the slurry of the present invention.

Similarly in wellbore cleanout operations, for example, water containing an EHRC can circulate in the wellbore and form slurry with debris in situ. The debris is subsequently transported out of the wellbore as slurry. The fluid is re-useable after separation from the debris.

For transporting particulates through pipelines slurry can be prepared by mixing the ingredients and then pumping the slurry through the pipeline.
CLAIMS:

1. An aqueous slurry composition, comprising
   (a) an aqueous liquid;
   (b) particulates; and
   (c) a chemical compound for rendering the surface of the particulates extremely hydrophobic.

2. The aqueous slurry composition of claim 1 wherein the size of the particulates is in the range of 10-100 US mesh.

3. The aqueous slurry composition of claim 1 or 2 wherein the particulates are selected from a group consisting of sands, resin coated sands, ceramic, carbonate, bauxite, shale and coal particulates.

4. The composition of any one of claims 1 to 4, wherein the particulates are subterranean formation particulates.

5. The composition of any one of claims 1 to 4, wherein the chemical compound is selected from a group consisting of organosilanes, organosiloxanes, fluoro-organosilanes, fluoro-organosiloxanes and fluoro-organic compounds.

6. The composition of any one of claims 1 to 4, wherein the chemical compound is an organosilane having the formula
   \[ R_n \text{Si}X(4-n) \]
   wherein \( R \) is an organic radical having 1-50 carbon atoms that may possess a functionality containing N, S, or P moieties that imparts desired characteristics, \( X \) is a halogen, alkoxy, acyloxy or amine and \( n \) has a value of 0-3.
7. The composition of any one of claims 1 to 4, wherein the chemical compound is selected from a group consisting of:

\[
\begin{align*}
    &\text{CH}_3\text{SiCl}_3, \text{CH}_2\text{CH}_2\text{SiCl}_3, \text{(CHs)}_2\text{SiCl}_2, \text{(CH}_2\text{CH}_2)_2\text{SiCl}_2, \text{(C}_6\text{Hs})_2\text{SiCl}_2, \\
    &\text{(C}_6\text{Hs})_2\text{SiCl}_3, \text{(CH}_3)_3\text{SiCl}, \text{CH}_3\text{HSiCl}_2, \text{(CH}_3)_2\text{HSiCl}, \text{CH}_3\text{SiBr}_3, \\
    &\text{(C}_6\text{Hs})_2\text{SiBr}_3, \text{(CH}_3)_2\text{SiBr}_2, \text{(CH}_3\text{CH}_2)_2\text{SiBr}_2, \text{(C}_6\text{Hs})_2\text{SiBr}_2, \text{(CH}_3)_3\text{SiBr}, \text{CH}_3\text{HSiBr}_2, \\
    &\text{(CHs)}_2\text{HSiBr}, \text{Si(OCH}_3)_4, \text{CH}_3\text{Si(OCH}_3)_3, \text{CH}_3\text{Si(OCH}_2\text{CHs)}_3, \\
    &\text{CH}_3\text{Si(OCH}_2\text{CH}_2\text{CH}_3)_3, \text{CH}_3\text{Si}[\text{O(CH}_2\text{CH}_3)_3, \text{CH}_3\text{CH}_2\text{Si(OCH}_2\text{CH}_3)_3, \\
    &\text{C}_6\text{Hs}(\text{OCH}_3)_3, \text{C}_6\text{HsCH}_2\text{Si(OCH}_3)_3, \text{C}_6\text{HsSi(OCH}_2\text{CH}_3)_3, \text{CH}_2=\text{CHCH}_2\text{Si(OCHs)}_3, \\
    &\text{(CH}_3)_2\text{Si(OCH}_3)_2, \text{(CH}_2=\text{CHSi(CHs)}_2\text{Cl}, \text{(CH}_3)_2\text{Si(OCH}_2\text{CH}_3)_2, \\
    &\text{(CH}_3\text{CH}_2\text{Si(OCH}_2\text{CH}_2\text{CHs)}_2, \text{(CHs)}_2\text{Si[O(CH}_2\text{sCHs)}_2, \text{(CHsCH}_2)_2\text{Si(OCH}_2\text{CH}_3)_2, \\
    &\text{(CH}_3\text{CH}_2\text{Si(OCH}_3)_2, \text{(CHsCH}_2)_2\text{Si(OCH}_2\text{CH}_3)_2, \text{(C}_6\text{Hs})_2\text{Si(OCH}_2\text{CH}_3)_2, \\
    &\text{(CHs)}_2\text{HSi(OCH}_3, \text{CH}_3\text{Si(OCH}_2\text{CH}_2\text{CHs)}_3, \text{CH}_2=\text{CHCH}_2\text{Si(OCH}_2\text{CH}_2\text{OCH}_3)_2, \\
    &\text{(C}_6\text{Hs})_2\text{Si(OCH}_2\text{CH}_2\text{OCH}_3)_3, \text{(CHs)}_2\text{Si(OCH}_2\text{CH}_2\text{OCH}_3)_2, \\
    &\text{(C}_6\text{Hs})_2\text{Si(OCH}_2\text{CH}_2\text{OCH}_3)_2, \text{(CHs)}_2\text{Si(OCH}_2\text{CH}_2\text{OCH}_3)_2, \\
    &\text{(C}_6\text{Hs})_2\text{Si(OCH}_2\text{CH}_2\text{OCH}_3)_2, \text{(CHs)}_2\text{Si(OCH}_2\text{CH}_2\text{OCH}_3)_2, \\
    &\text{(C}_6\text{Hs})_2\text{Si(OCH}_2\text{CH}_2\text{OCH}_3)_2, \text{CH}_3\text{Si(\text{CH}_3\text{COO})}_3, \text{3-aminotriethoxysilane}, \\
    &\text{methyldiethylchlorosilane, butyldichlorosilane, diphenyldichlorosilane, vinyltri-} \\
    &\text{chlorosilane, methyltrimethoxysilane, vinyltriethoxysilane, vinyltris(} \text{methoxyethoxy})\text{silane, methacryloxypropyltrimethoxysilane}, \\
    &\text{glycidoxypropyltrimethoxysilane, aminopropyltriethoxysilane, divinyl-2-methoxysilane, ethyltributoxysilane, isobutyltrimethoxysilane,} \\
    &\text{hexyltrimethoxysilane, n-octyltriethoxysilane, dihexyldimethoxysilane, octadecyl-} \\
    &\text{triethylsiloxane, octadecyltrimethoxysilane,}
\end{align*}
\]
octadecyldimethylchlorosilane, octadecyldimethylmethoxysilane and quaternary ammonium silanes including S-(trimethoxysilyloxy)propyldimethyloctadecyl ammonium chloride, 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium bromide, 3-(trimethylethoxysilyl)propyldidecylmethyl ammonium chloride, triethoxysilyl soyapropyl dimonium chloride, 3-
(trimethylethoxysilyl)propyldidecylmethyl ammonium bromide, 3-
(trimethylethoxysilyl)propyldidecylmethyl ammonium bromide, triethoxysilyl soyapropyl dimonium bromide, (CH$_3$O)$_3$Si(CH$_2$)$_3$P+(CeH$_5$)$_3$Cl,

(CH$_3$O)$_3$Si(CH$_2$)$_3$P+(C$_6$H$_5$)$_3$Br, (CH$_3$O)$_3$Si(CH$_2$)$_3$P+(CH$_3$)$_3$Cl$^-$,

(CH$_3$O)$_3$Si(CH$_2$)$_3$P+(C$_6$H$_3$)$_3$Cr, (CH$_3$O)$_3$Si(CH$_2$)$_3$N+(CH$_3$)$_2$C$_4$H$_9$Cl,

(CH$_3$O)$_3$Si(CH$_2$)$_3$N+(CH$_3$)$_2$CH$_2$C$_6$H$_5$Cr$_1$ (CH$_3$O)$_3$Si(CH$_2$)$_3$N+(CH$_3$)$_2$CH$_2$CH$_2$OHCr,

(CH$_3$O)$_3$Si(CH$_2$)$_3$N+(C$_2$H$_5$)$_3$Cr, (C$_2$H$_5$O)$_3$Si(CH$_2$)$_3$N+(CH$_3$)$_2$C$_18$H$_37$C$^-$.

8. The composition of any one of claims 1 to 4, wherein the chemical compound is an organosiloxane.

9. The composition of claim 8, wherein the organosiloxane is selected from a group consisting of polyalkylsiloxanes, cationic polysiloxane, amphoteric polysiloxanes, sulfate polysiloxanes, phosphate polysiloxanes, carboxylate polysiloxanes, sulfonate polysiloxanes, thiosulfate polysiloxanes, hexamethyldicyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, hexamethyldisiloxane, hexaethyldisiloxane, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, octamethyltrisiloxane and decamethyltetrasiloxane.
10. The composition of claim 8, wherein the organosiloxane is selected from a group consisting of hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, hexamethyldisiloxane, hexaethyldisiloxane, 1,3-divinyl-1,3,3-tetramethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane.

11. The composition of claim 8, wherein the organosiloxane is a polyalkylsiloxane.

12. The composition of claim 8, wherein the organosiloxane is a cationic polysiloxane.

13. The composition of claim 8, wherein the organosiloxane is a quaternary polysiloxane.

14. The composition of claim 8, wherein the organosiloxane is an amphoteric polysiloxane.

15. The composition of claim 8, wherein the organosiloxane is a betaine polysiloxane.

16. The composition of claim 8 wherein the organosiloxane is selected from a group consisting of sulfate polysiloxane, sulfonate polysiloxane, phosphate polysiloxane, carboxylate polysiloxane and thiosulfate polysiloxane.

17. The composition of claim 8, wherein the organosiloxane is a cationic polysiloxane having the formula
wherein each of R_i to R_6 and R_8 to R_{10}, represents alkyl containing 1-6 carbon atoms, typically a methyl group, R_7 represents a quaternary group and is associated with an anionic ion and may have a hydroxyl group and may be interrupted by an oxygen atom, an amino group or an amide group, and m and n are from 1 to 200.

18. The composition of claim 8, wherein the organosiloxane is a betaine polysiloxane having the formula

\[
\begin{align*}
   R_1 & \quad Si \quad O \quad Si \quad O \quad Si \quad R_{10} \\
   & \quad R_2 \quad R_4 \quad [O_\text{m}] \quad R_6 \quad R_8 \\
   & \quad R_3 \quad R_5 \quad [\text{Si}_\text{n}] \\
\end{align*}
\]

wherein each of R_i to R_6 and R_8 to R_{10}, represents alkyl containing 1-6 carbon atoms, typically a methyl group, R_7 represents an organic betaine group and may have a hydroxyl group and may be interrupted by an oxygen atom, an amino group or an amide group, and m and n are from 1 to 200.

19. The composition of claim 8, wherein the organosiloxane is according to the formula

\[
\begin{align*}
   R_{11} & \quad Si \quad O \quad Si \quad O \quad Si \quad R_{18} \\
   & \quad R_{12} \quad R_{14} \quad [O_\text{m}] \quad R_{16} \\
   & \quad R_{13} \quad R_{15} \quad [\text{Si}_\text{n}] \\
\end{align*}
\]

where R_{i_2} to R_{i_7}, each represents alkyl containing 1-6 carbon atoms, typically a methyl group, R_{n} and R_{i_8}, each represents an organic betaine group and may have a hydroxyl group and may be interrupted by an oxygen atom, an amino group or an amide group and m is 1 to 200.
20. The composition of claim 8, wherein the organosiloxane is according to the formula

\[
\begin{align*}
\text{R}_{11} \quad \text{Si} \quad 
\begin{array}{c}
\text{R}_{12} \\
\text{R}_{13}
\end{array}
\quad \text{O} \quad 
\begin{array}{c}
\text{Si} \\
\text{R}_{15}
\end{array}
\quad \text{O} \quad 
\begin{array}{c}
\text{Si} \\
\text{R}_{17}
\end{array}
\quad \text{R}_{16} \\
\text{R}_{18}
\end{align*}
\]

where \( R_{12} \) to \( R_{17} \) each represents alkyl containing 1-6 carbon atoms, typically a methyl group, \( R_n \) and \( R_{18} \) each independently represents an organic quaternary group and is associated with an anionic ion and may have a hydroxyl group and may be interrupted by an oxygen atom, an amino group or an amide group and \( m \) is 1 to 200.

21. The composition of any one of claims 1 to 20 further including a gas.

22. A fracturing fluid including the slurry composition according to any one of claims 1 to 21.

23. A gravel-pack fluid including the slurry composition according to any one of claims 1 to 21.

24. A drilling fluid including the slurry composition according to any one of claims 1 to 21.

25. The use of the slurry composition according to any one of claims 1 to 21 for transporting particulates through a pipeline.

26. The use of the slurry composition according to any one of claims 1 to 21 in a well service operation.

27. A method of making an aqueous slurry composition comprising the steps
(a) treating particulates with a chemical compound to render the particulate surface extremely hydrophobic, and then

(b) mixing the treated particulates with an aqueous liquid to make an aqueous slurry.

28. A method for making an aqueous slurry composition comprising steps of mixing

(a) an aqueous liquid;

(b) particulates; and

(c) a chemical compound for rendering the surface of the particulates extremely hydrophobic.

29. The method of claim 27 or 28 wherein the size of particulates is in the range of 10-100 US mesh.

30. The method of any one of claims 27 to 29 wherein the particulates are selected from a group consisting of sands, resin coated sands, ceramic, carbonate, bauxite, shale and coal particulates.

31. The method of any one of claims 27 to 30, further including the step of mixing the slurry with a gas.

32. The method of any one of claims 27 to 31 wherein the chemical compound is selected from a group consisting of organosilanes, organosiloxanes, fluoro-organosilanes, fluoro-organosiloxanes and fluoro-organic compounds.

33. The method of any one of claims 27 to 31 wherein the chemical compound is an organosilane having the formula
$R_nSiX(4-n)$

wherein $R$ is an organic radical having 1-50 carbon atoms that may possess a functionality containing $N$, $S$, or $P$ moieties that imparts desired characteristics, $X$ is a halogen, alkoxy, acyloxy or amine and $n$ has a value of 0-3.

34. The method of any one of claims 27 to 31 wherein the chemical compound in claim 21 is an organosiloxane selected from a group consisting of polyalkylsiloxanes, cationic polysiloxanes, amphoteric polysiloxanes, sulfate polysiloxanes, phosphate polysiloxanes, carboxylate polysiloxanes, sulfonate polysiloxanes, thiosulfate polysiloxanes, hexamethylocyclotrisiloxane, octamethylocyclotetrasiloxane, decamethylocyclopentasiloxane, hexamethylidisiloxane, hexaethylidisiloxane, 1,3-divinyl, 1,3,3-tetramethyldisiloxane, octamethyltrisiloxane and decamethyltetrasiloxane.

35. The method of any one of claims 27 to 31 wherein the chemical compound is a polyalkylsiloxane.

36. The method of any one of claims 27 to 31 wherein the chemical compound is a cationic polysiloxane.

37. The method of any one of claims 27 to 31 wherein the chemical compound is a quaternary polysiloxane.

38. The method of any one of claims 27 to 31 wherein the chemical compound is an amphoteric polysiloxane.

39. The method of any one of claims 27 to 31 wherein the chemical compound is a betaine polysiloxane.
40. The method of any one of claims 27 to 31 wherein the chemical compound is selected from a group consisting of sulfate polysiloxane, sulfonate polysiloxane, phosphate polysiloxane, carboxylate polysiloxane and thiosulfate polysiloxane.

41. The method of any one of claims 27 to 40 further including the step of mixing a surfactant with the slurry composition.

42. The slurry composition of any one of claims 1 to 21 further including a surfactant.

43. The fracturing fluid of claim 22 further including a surfactant.

44. The gravel-pack fluid of claim 23 further including a surfactant.

45. The drilling fluid of claim 24 further including a surfactant.

46. A wellbore cleanout fluid including the slurry composition according to any one of claims 1 to 21.