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PRODUCTRICES D'HYDROCARBURES

(54) Title: TREATING SHALE AND CLAY IN HYDROCARBON PRODUCING FORMATIONS

(57) Abrégé/Abstract:

Clay is stabilized in the drilling of wells and other formation treatment for hydrocarbon production by the addition to the drilling or other fluid of potassium formate together with a cationic formation control additive.



Abstract

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Treating Shale and Clay in Hydrocarbon Producing Formations

Technical Field

This application relates to the drilling of wells in the production of oil, gas and other fluids from underground formations, and particularly to the stabilization of boreholes drilled for the production of hydrocarbons. It includes the treatment of shale and clay *in situ* to prevent swelling caused by the absorption of water from drilling fluids.

Background of the Invention

A good description of the problem which this invention addresses in the context of formation drilling may be found in an article by Thomas W. Beihoffer et al in the May 16, 1992 Oil & Gas Journal, page 47 et seq., entitled "Cationic Polymer Drilling Fluid Can Sometimes Replace Oil-based Mud." As stated therein, "(S)hales can become unstable when they react with water in the drilling fluid. These reactive shales contain clays that have been dehydrated over geologic time by overburden pressure. When the formation is exposed, the clays osmotically imbibe water from the drilling fluid. This leads to swelling of the shale, induced stresses, loss of mechanical strength, and shale failure." Shale crumbling into the borehole ("sloughing") can ultimately place a burden on the drill bit which makes it impossible to retrieve.

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Salts such as potassium chloride have been widely used in drilling treatments to convert the formation material from the sodium form by ion exchange to, for example, the potassium form which is less vulnerable to swelling; also the use of high concentrations of potassium salts affects the osmotic balance and tends to inhibit the flow of water away from the high potassium salt concentrations into the shale. However, it is difficult to maintain the required high concentrations of potassium salts in the drilling fluids. In addition, the physical introduction of such salts causes difficulties with the preparation of the viscosifying materials typically used for drilling. Inorganic salts can also have a harmful effect on the environment if released.

As background for the present disclosure, I have assembled prior art references representative of three general types of amine and quaternary ammonium cation sources which have been suggested for clay treatment in hydrocarbon recovery. These are (a) single-site quaternaries and amines, (b) compounds having a few (two to about six) amine or quaternary ammonium cation sites, which I have called "oligocationic", and (c) quaternary ammonium or amine polymers, which may have from about six to thousands of cationic sites. The cationic materials described in these references are representative of materials useful in my invention. The following are all U.S. patents.

- A. Single-Site Quaternaries and Amines: Brown 2,761,835, Brown 2,761,840, Brown 2,761,836, Himes et al 4,842,073, Thomas and Smith 5,211,239.
- B. Oligocationics: Brown 2,761,843; Krieg 3,349,032.
- C. Polycationics: Borchardt et al 4,447,342, McLaughlin et al 4,374,739, McLaughlin et al 4,366,071.

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Brown (U.S. Patent No. 2,761,835), found that a clay body can be stabilized to impart or maintain satisfactory permeability to fluids, improved mechanical strength and increased resistance to chemical attack by treating such clay body with substituted ammonium ions, derived from aliphatic nitrogen compounds, selected from the group consisting of di-alkyl-substituted ammonium ions wherein each alkyl substituent has a total of 3 to 8 carbon atoms, with the longest straight chain, starting with the carbon attached to the nitrogen, having 3 to 7 carbon atoms, preferably 3 to 6 carbon atoms; tri-alkyl-substituted ammonium ions wherein each alkyl substituent has a total of 3 to 8 carbon atoms, with the longest straight chain, starting with the carbon attached to the nitrogen, having 3 to 7 carbon atoms, preferably 3 to 6 carbon atoms; and tetra-alkyl-substituted ammonium ions wherein each alkyl substituent has a total of 2 to 8 carbon atoms, with the longest straight chain, starting with the carbon attached to the nitrogen, having 2 to 7 carbon atoms, preferably 3 to 6 carbon atoms. The di-alkyl, tri-alkyl and tetra-alkyl ammonium ions can be symmetrical or unsymmetrical.

While the substituted ammonium ions defined above are effective clay-stabilizing agents, the parent basic nitrogen compounds from which the substituted ammonium ions are derived have essentially no clay-stabilizing action. Di-, tri-, and tetra-substituted ammonium ions having alkyl substituents of 8 or more carbon atoms in a straight chain form clay complexes which can swell or disperse in organic liquids, this property being more pronounced the greater the length of the alkyl chain. They are thus of limited utility in stabilizing clay bodies which may come in contact with organic liquids. Di-, tri-, and tetra-substituted ammonium ions having alkyl substituents with 8 or more carbon atoms in a straight chain tend to produce an increase in clay volume forming a clay complex which may result in swelling of unhydrated clay and only little or no shrinking of hydrated swollen clay.

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The substituted ammonium ions can be obtained, among other ways, from salts prepared by reacting an appropriate basic nitrogen compound of the class described with an acid, preferably one whose anionic competent will not form a precipitate with ions associated with substances such as aqueous fluids with which the substituted ammonium salt may come in contact. Thus, if the fluids contain a significant concentration of alkaline earth ions, it is inadvisable to employ salts whose anionic component may be sulfate, oxalate, etc., since a precipitate can result. Among the compounds which can be employed in preparing the salts are hydrochloric acid, hydrobromic acid, nitric acid, lactic acid, citric acid, salicylic acid, etc., lower fatty acids such formic, acetic, propionic, etc., and propyl bromide, ethyl bromide, isopropyl iodide, etc. Among the salts which are satisfactory for use in accordance with Brown's invention are di-n-propylammonium chloride, di-n-propylammonium acetate, di-n-propylammonium citrate, n-propylammonium acetate, di-n-propylammonium citrate, n-propyl-n-butylammonium chloride, di-n-butylammonium chloride, di-n-butylammonium acetate, di-n-butylammonium lactate, di-n-butylammonium propionate, diisobutylammonium chloride, diisobutylammonium formate, diisobutylammonium salicylate, di-n-amylammonium chloride, diisoamylammonium chloride, di-2-methylbutylammonium chloride, di-n-hexylammonium chloride, di-n-heptylammonium chloride, di-n-heptylammonium acetate, tri-n-propylammonium chloride, tri-n-propylammonium iodide, tri-n-butylammonium chloride, tri-n-butylammonium acetate, tri-n-butylammonium nitrate, triisobutylammonium chloride, tri-n-amylammonium chloride, triisoamylammonium chloride, tri-n-hexylammonium chloride, tri-n-heptylammonium chloride, tetraethylammonium chloride, tetraethylammonium bromide, tetra-n-propylammonium chloride, tetra-n-butylammonium chloride, tetra-n-butylammonium iodide, tetra-n-butylammonium acetate, tetraisobutylammonium chloride, tri-n-butyl-3-methylbutylammonium iodide,

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tetraisoamylammonium chloride, tetraisoamylammonium iodide, tetra-n-hexylammonium chloride, and tetra-n-heptylammonium chloride.

Similar results were obtained in Brown, U.S. Patent No. 2,761,840 and 2,761,836. Brown also discloses additional suitable salts in U.S. Patent No. 2,761,843, namely dipropylenetriamine trihydrochloride, dipropylenetriamine trihydrobromide, triethylenetetramine tetrahydrochloride, 3-dimethylaminopropylamine dihydrochloride, tetra-ethylenepentamine pentaacetate, 3-isopropylaminopropylamine dihydrochloride, 3-isopropylaminopropylamine dilactate, 3-dimethylaminopropylamine dinitrate, tetraethylenepentamine pentahydrochloride, 3-diethylaminopropylamine dicitrate, 1,10-diaminodecane dihydrochloride, 1,10-diaminodecane disalicylate, 2-amino-5-diethylaminopentane dihydrochloride, 2-amino-5-diethylaminopentane dipropionate, 1,8-diaminooctane dihydrochloride, 1,8-diaminooctane diformate, 1,6-diaminohexane dihydrochloride, 1,6-diaminohexane diiodide, N,N-diethylethylenediamine dihydrochloride, N-n-butylpoly-4-vinylpyridine bromide, poly-4-vinylpyridine bromide and polyvinylamine acetate.

Himes and Vinson (U.S. Patent No. 4,842,073) found that a fluid additive comprising at least one member selected from the group consisting of N-alkylpyridinium halides, N,N-dialkylmorpholinium halides, tetralkylammonium halides, N,N,N-trialkylphenylammonium halides, N,N,N-trialkylbenzylammonium halides and the alkyl quaternary ammonium salt of a 2 mole oligomer of epihalohydrin, wherein the alkyl radical is selected from the group consisting of methyl, ethyl, propyl and butyl radicals, can be admixed with an aqueous fluid to be utilized in the stimulation of a subterranean formation. Alternatively, the halide anion may be replaced by any other anion which is compatible with the subterranean formation to be treated and the constituents of the stimulation fluid. The additive is admixed in an effective amount

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with the aqueous stimulation or treatment fluid whereby clay swelling is reduced and formation permeability is substantially maintained upon contact of the aqueous fluid with the formation.

Hydraulic fracturing has been utilized for many years to stimulate the production of oil, gas or other formation fluids from subterranean formations. In hydraulic fracturing, a suitable fluid is introduced into a subterranean formation by way of a wellbore under conditions of flow rate and pressure which are at least sufficient to create or extend a fracture into a desired portion of the formation. The fracturing fluid normally carries in it a proppant which is forced into the fracture or fractures to keep the broken formation from closing completely once the pressure is released. Various fluids have been utilized in hydraulic fracturing, however, most fluids utilized today are aqueous-based liquids.

The fracturing fluid of Himes and Vinson is prepared by admixing a quantity of a polymeric gelling agent with an aqueous liquid. Generally, the gelling agent is a solvatable polysaccharide. The solvatable polysaccharides include galactomannan gums, glucomannan gums, cellulose derivatives and the like. The fracturing fluid also may include a crosslinking agent for the gelling agent as well as other additives. For example, the fluid can contain bactericides, breakers, iron control agents, foaming agents such as surfactants, gases or liquified gases, stabilizers and the like. The preparation of such fluids and the various additives are well known to individuals of ordinary skill in the art.

In addition to the foregoing additives, most aqueous fracturing fluids also include a formation control additive. The formation control additive generally utilized has been a solubilizable salt such as potassium chloride, ammonium chloride, sodium chloride,

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calcium chloride or the like. These salts can be difficult to admix under actual conditions of use or can have detrimental effects upon fluid properties such as reducing the viscosity achieved by a gelling agent in the aqueous fluid in comparison to hydration of the gelling-agent in fresh water. These compounds have been utilized, however, because of the ion-exchange properties of the clays present in the subterranean formations to be treated and the ability of these chemicals to provide some degree of formation stabilization through ion-exchange with the clays.

Among the clays which may be present originally in natural geological formations or which may have been introduced therein and which can be effectively treated are included clay minerals of the montmorillonite (smectite) group such as montmorillonite, saponite, nontronite, hectorite, and sauconite; the kaolin group such as kaolinite, nacrite, dickite, and halloysite; the hydrous-mica group such as hydrobiotite, glauconite, illite and bramallite; the chlorite group such as chlorite and chamosite; clay minerals not belonging to the above groups such as vermiculite, attapulgite, and sepiolite, and mixed-layer varieties of the above minerals and groups. The clay content of the formations can be comprised substantially of a single species of clay mineral, or of several species, including the mixed-layer types of clay. Of the clay minerals commonly encountered in natural geological formations which can be productive of the difficulties herein noted and which can be treated effectively are clay minerals selected from the class consisting of the montmorillonite group, hydrous mica group, chlorite group, kaolin group and mixed layer types containing several of the classes.

Clays can swell and/or disperse, disintegrate or otherwise become disrupted in the presence of aqueous fluids. A clay which swells is not limited to expanding lattice-type clays but includes all those clays which can increase in bulk volume with or

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without dispersing, disintegrating or otherwise becoming disrupted when subjected to contact with aqueous solutions such as water, certain brines, etc. Certain clays can also disperse, disintegrate or otherwise become disrupted without swelling in the presence of aqueous solutions such as water, certain brines, emulsions containing water or certain brines, and the like. Some clays in the presence of such aqueous solutions will expand and be disrupted to the extent that they will become unconsolidated and move into a borehole. Formations which consist largely of clay can develop pressures on the order of several thousand pounds per square inch upon absorbing water in a confined space.

The clay materials defined above occur as minute, plate-like, tube-like and/or fiber-like particles having an extremely large surface area compared to that of an equivalent quantity of a granular material such as sand. This combination of small size and great surface area results in a high surface energy with attendant unusual surface properties and extreme affinity for surface-active agents. The structure of some of these clays, as for instance montmorillonite, can be pictured as a stack of sheet-like three-layer lattice units which are weakly bonded to each other and which are expanded in the "c" crystallographic direction by water or other substances which can penetrate between the sheets and separate them. Montmorillonite has a cationexchange capacity of from about 90 to 130 milliequivalents per 100 grams of pure clay, illite from about 20 to 40 milliequivalents, and kaolinite from about 5 to 15 milliequivalents.

The properties of the clays vary widely with the cations occupying the base-exchange positions or sites. A "base-exchange position or site" can be defined as an area, in this instance on a clay crystal, which has associated with it an exchangeable cation. Among the cations which are generally found on the base-exchange position or site can be mentioned sodium, potassium, calcium, magnesium, iron, hydrogen, etc. These cations

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are believed to be held to the clay surface by ionic forces.

The cations occupying the base-exchange sites on the clay can be those originally present or cations finding their way to the base-exchange position from the liquids in contact therewith. Accordingly, the nature and concentrations of ions in the water in contact with the clay can determine the cations occupying the base exchange sites. In most oil well formations the natural waters associated therewith contain sodium as the predominant cation, with calcium, magnesium and other cations present in much smaller quantities. Since the base-exchange positions on the clay are occupied by cations, in many cases the cation will be sodium when natural ground waters such as those described above are associated therewith. Unfortunately, however, as for example in the case of the sodium form of montmorillonite, these clay minerals swell in the presence of water or certain brines and can, in some instances, exert pressures up to thousands of pounds per square inch. Thus, dependent upon the amount of water absorbed, the clay can change to a rigid paste or a gelatinous mass, or if sufficient water is present, the clay can disperse completely into the aqueous phase.

The swelling or dispersion of the clays can significantly reduce the permeability of the formation. The use of the foregoing salts as formation control additives has not eliminated formation damage as a result of permeability reduction, but merely has attempted to reduce or minimize such damage.

Himes and Vinson found that the use of a formation control additive comprising at least one member selected from the group of quaternary ammonium halides consisting of N-alkylpyridinium halides such as N-methylpyridinium halides, N,N-dialkylmorpholinium halides such as, N,N-dimethylmorpholinium halides, N,N,N-trialkylphenylammonium halides, such as N,N,N-trimethylphenylammonium halides,

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N,N,N-trialkylbenzylammonium halides such as N,N,N-trimethylbenzylammonium halides. The halide can comprise fluorine, chlorine, bromine or iodine. Alternatively, the halide anion may be replaced by any other anion which is compatible with the subterranean formation to be treated and the constituents of the stimulation fluid. The anion may comprise, for example, under appropriate circumstances nitrite, nitrate or sulfate.

The quaternary ammonium halides are admixed with the aqueous fracturing fluid in an effective amount to substantially stabilize the formation against permeability damage as a result of contact with the aqueous fracturing fluid. Preferably, the formation control additive of Himes and Vinson is admixed with the aqueous fracturing fluid in an amount of at least about 0.05 percent by weight of the fracturing fluid. Most preferably, the formation control additive is present in an amount of from about 0.1 to about 5 percent by weight of the aqueous fracturing fluid.

The formation control in Himes and Vinson additive can be admixed with the fracturing fluid at any time prior to contact of the fluid with the subterranean formation. In that the formation control additives are readily available as liquid solutions, they readily admix with the constituents of the aqueous fracturing fluid both prior to and subsequent to hydration of the gelling agent. The use of this formation control additives is particularly advantageous in stimulation treatments performed with liquid gel concentrates such as for example those described in U.S. Pat. Nos. 4,312,675; 4,435,217; 3,894,880; 3,894,879; and 4,466,890. The formation control additive is effective in treating a subterranean formation when transported in a carrier fluid such as a fracturing fluid having either an acid, alkaline or neutral pH. The formation control additive carrier may have a pH in the range of from about 1 to 11 without any significant detrimental effect upon the formation control additive.

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The formation control additive may be admixed with the constituents of aqueous liquid gel concentrate during its preparation whereupon it remains storage stable or admixed with the gel concentrate when the gelled fracturing fluid is prepared by introduction into a mixing vessel or blender together with the other fracturing fluid additives. The formation control additives of Himes and Vinson do not result in the mixing problems associated with previously used salts and do not appear to have any significant detrimental effect upon the hydration or ultimate yield of the gelling agent utilized to prepare the fracturing fluid.

Thomas and Smith (U.S. Patent No. 5,211,239) found that the permeability of subterranean formations may be maintained -- that is, fines present or released by the fracturing process can be prevented from clogging capillary fissures and clays can be inhibited from swelling and slowing the flow of fluids -- by including in the fracturing fluid an effective amount of a dimethyl diallyl ammonium salt.

The allyl ammonium salts employed by Thomas and Smith may be admixed with the aqueous fracturing fluid in an effective amount to substantially stabilize the formation against permeability damage as a result of contact with the aqueous fracturing fluid. The formation control additive allyl ammonium salt is generally admixed with the aqueous fracturing fluid in an amount of at least about 0.05 percent by weight of the fracturing fluid. Preferably the formation control additive is present in an amount of from about 0.1 to about 5 percent by weight of the aqueous fracturing fluid; most preferably about 0.2% to about 1%. The actual amount may be determined by estimates of the amount of clay in the formation using representative core samples in standard core flow testing as is known in the art.

In Thomas and Smith the allyl ammonium salt may be admixed with the fracturing

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fluid at any time prior to contact of the fluid with the subterranean formation. In that the allyl ammonium salt is readily available as a liquid solution, it is readily mixed with the constituents of the aqueous, fracturing fluid both prior to and subsequent to hydration of the gelling agent. The most commonly used gelling agents presently are polysaccharides and in particular natural guar, hydroxypropyl guar, hydroxyethylcellulose, and xanthan gum.

Examples of suitable quaternary compounds are found in Krieg, U.S. Patent No. 3,349,032.

McLaughlin et al., U.S. Patent No. 4,366,071, describe suitable organic polycationic polymers. The organic polycationic polymers of McLaughlin can generally be considered quaternary polymers with nitrogen or phosphorous as the quaternary or cationic atom with an aliphatic, cycloaliphatic or aromatic chain. Trivalent or tertiary sulfur can be substituted for the quaternary nitrogen or phosphorous in the polymers. The cationic atom to carbon atom ratio is preferably about 1:2 to 1:36 and the molecular weight is above about 1,000. The organic polycationic polymer is polar and therefore generally soluble or readily dispersible in polar solvents or carrier fluids such as an aqueous media or an alcohol, or another substitute hydrocarbon can be used as the carrier fluid where it is desirable to avoid contact between water and the permeable mass or formation to be treated. Examples of these polycationic polymers include polyethyleneamines, polyvinylpyridinium salts, or polyallylammonium salts.

Other suitable cationic organic polymers are recited in Borchardt, U.S. Patent No. 4,447,342.

Summary of the Invention

My invention includes the use of combinations of potassium formate with various cationic materials, for the treatment of clay and shale in subterranean formations during drilling and otherwise for the stabilization of clay and clay-containing shale. It should be noted that all of the above identified patents address problems similar to the problem I address. Each of the patents employs cationic formation control additives for drilling fluids to help control the swelling and sloughing of shale and clay contacted by aqueous drilling and other formation treating fluids. The contexts of use of such additives and the techniques for employing them as described in those patents are entirely consistent with and compatible with my invention. That is, I employ my own combination of additives in drilling fluids and otherwise to treat shale and clay to control swelling and sloughing.

It will be seen from the prior art references described above that the three general types of cationic materials I may use in my invention for the stabilization of clay in subterranean formations are single-site cationics, oligocationics, and polycationics. Together they may be referred to herein as “cationic formation control additives.” Although cationics derived from sulfur, phosphorous and other elements capable of forming water-soluble cationic sites are effective and included in my invention, I prefer to use amine or ammonium-based cations. Thus the cationic portion of my clay treatment composition is preferably an amine or ammonium based (succinctly, “nitrogen-based”) cationic material. I may use any of the cationic materials described in the above identified patents.

The single site amine and quaternaries useful as cationic formation control additives in my invention include di-, tri, and tetra- alkyl substituted amine and ammonium

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compounds wherein the alkyl groups include from 3 to 8 carbon atoms (Brown 2,761,835); substituted pyridine, pyridinium, morpholine and morpholinium compounds having from 1 to 6 carbon atoms in one or more substituent groups (Brown 2,761,840), additional heterocyclic nitrogen compounds such as histamine, imidazoles and substituted imidazoles, piperazines, piperidines, vinyl pyridines, and the like as described in Brown 2,761,836, the trialkylphenylammonium halides, dialkylmorpholinium halides and epihalohydrin derivatives described by Himes et al in the 4,842,073 patent, and the allyl ammonium compounds of the formula $(\text{CH}_2=\text{CHCH}_2)_n\text{N}^+(\text{CH}_3)_{4-n} \text{X}^-$ where X^- is any anion which does not adversely react with the formation or the treatment fluid, described by Thomas and Smith in US Patent 5,211,239, and is preferably a halide ion, and n is an integer from 1 to 4. Preferred single site quaternaries are diallyl dimethyl ammonium chloride (that is, the above formula where $n=2$ and X^- is Cl^-), preferably having a molecular weight from about 1000 to about 500,000, and tetramethyl ammonium chloride, sometimes referred to as TMAC.

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Oligocationics useful as cationic formation control additives in my invention include di- and polyamines (up to 100 nitrogens) substituted with alkyl groups having up to 12 carbon atoms (one or more of the nitrogens may be quaternized) as described by Brown in US Patent 2,761,843, and polyquaternaries described by Krieg in US Patent 3,349,032, namely alkyl aryl, and alkaryl bis- and polyquaternaries wherein two quaternary ammonium nitrogens are connected by various connecting groups having from 2-10 carbon atoms.

Polyquaternary (cationic) formation control additives useful in my invention include those described by McLaughlin in the 4,366,071 and 4,374,739 patents, namely polymers containing repeating groups having pendant quaternary nitrogen atoms wherein the quaternizing moieties are usually alkyl groups but which can include other groups capable of combining with the nitrogen and resulting in the quaternized state. I may also use any of the numerous polymers including quaternized nitrogen atoms which are integral to the polymer backbone, and other polymers having repeating quaternized units, as described by Borchardt in the '342 patent. Nitrogen-based cationic moieties may be interspersed with and/or copolymerized with up to 65% by weight (preferably 1% to 65% by weight) nonionics such as acrylamide and even some anionics such as acrylic acid or hydrolyzed acrylamide. Molecular weights of the polymers may be quite high – up to a million or more. Such copolymers are included in my definition of polycationic formation control additives useful in my invention.

Preferred anions for association with the quaternized nitrogen atoms are halide anions, particularly chloride ions, which readily dissociate in the aqueous drilling or other formation treatment fluid, but any anions, including formate anions, may be used

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which will not interfere with the purposes of the formation treatment. Persons skilled in the art may wish to review the various anions mentioned in the above patents.

Thus it is seen that a cationic formation control additive useful in my invention is a material having from one to hundreds or thousands of cationic sites, generally either amines or quaternized amines, but may include other cationic or quaternized sites such as phosphonium or sulfonium groups.

I employ potassium formate together with a cationic formation control additive. The potassium formate may be added to the formation treating or drilling fluid before or after the cationic formation control additive, or may be made in situ by the reaction of potassium hydroxide and formic acid. The potassium hydroxide and formic acid may be added in any order, separately or together, before or after the addition of the cationic formation control additive, and need not be added in exact molar proportions. Any effective amount of the combination of potassium formate and formation control additive may be used, but I prefer to use ratios of potassium formate to formation control additive of 25:75 to 75:25 by weight in the solution, in combined concentrations of at least 0.001% by weight in the drilling or other formation treatment fluid.

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Following are results from a clay pack flow test and a capillary suction test.

Clay Pack Flow Test							
Volume (higher the better)							
Test products	Elapsed time →	start	1 minute	3 minutes	5 min	10 min	CST time
Fresh water		5	15	17	23	25	225.2
2% KCl		15	87	175			102
1% KCl and 12 GPT KCOOH		19	80	132	172		36.1
poly(DADMAC) 2 GPT		26	90	140	185		38.3
poly(DADMAC) + KCOOH 2 GPT		21	83	132	170	212	45.6
poly(DADMAC) 1 GPT		22	52	72	86	112	63.8
poly(DADMAC) + KCOOH 1 GPT		21	74	112	140	179	40.9
poly(DADMAC) 0.5 GPT		5	21	28	34	47	224.6
poly(DADMAC) + KCOOH 0.5 GPT		18	55	80	107	146	58.6
LMWP (DADMAC) 2 GPT		14	42	64	82	107	68.4
LMWP (DADMAC) 2 GPT + KCOOH		19	64	83	118	156	57
HMWP (DADMAC/AA) 2 GPT		8	26	38	48	60	165.8
HMWP (DADMAC/AA) + KCOOH 2 GPT		17	48	71	88	114	60.6
Monomer (DADMAC) 2 GPT		2	17	22	30	42	239.6
KCOOH (37%) 2 GPT		7	25	31	41	51	168.7
Champion TMAC 2 GPT		1	36	63	75	109	146.4
Champion TMAC 1 GPT		3	23	33	39	47	263.9
TMAC 1 GPT + 12 GPT KCOOH		15	59	95	124	172	68.9

Poly(DADMAC) = 25% poly(diallyldimethyl ammonium chloride)

TMAC = 25% by weight tetramethyl ammonium chloride

GPT = gallons of the test additive(s) solution per thousand gallons of formation treatment (drilling) fluid

HMWP = 15.5% by weight of the indicated high molecular weight polymer

LMWP = 14.5% by weight of the indicated low molecular weight polymer

KCOOH = 18% by weight aqueous solution

From the above table, it can be seen that the addition of potassium formate to the formation control additives improved the results considerably. In the clay pack flow test, where the higher volumes at a given time indicate better clay stability, the

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addition of a small amount of potassium formate increased the volume throughput for a given polymer concentration. In fact, adding the potassium formate improved the performance of a polymer more than using twice the concentration of the polymer alone. For example, the poly(DADMAC) at 1 GPT treatment had a volume at 10 minutes of 112 ml. The same polymer, when combined with potassium formate and treated at 0.5 GPT (half the original polymer concentration), had a volume of 146 ml, indicating better clay stability and a possible synergistic effect from the addition of the potassium formate.

Similar results are obtained from the CST data. In this test, a constant volume of treated fluid is flowed across a clay and filter medium. The lower the time for the volume to pass through, the better the clay stabilization. The addition of potassium formate lowers the CST time in nearly all cases, indicating a benefit in performance from the formate. The presence of potassium formate, as in the clay pack flow test, also indicates synergy with the polymer. The CST time for the poly(DADMAC) + potassium formate at 0.5 GPT is lower than the time for the higher concentration (1 GPT) of polymer alone. Thus, the addition of potassium formate is sufficiently beneficial to allow reducing the polymer by half, and still increase the performance.

In both the clay pack flow test and the CST, the polymer combinations with the potassium formate were also better than the effect of formate alone. The CST result and the clay pack flow test volume for the 2 GPT of 37% potassium formate (by itself) were both worse than even the low treatment levels of the polymer/formate combinations, but better than some of the polymer treatments alone. This indicates that, while the potassium formate is effective alone and better than some polymer-only treatments, its performance is enhanced when combined with the formation control additives.

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CLAIMS:

1. Method of reducing permeability damage in a subterranean formation from contact of a treatment fluid with said subterranean formation comprising contacting the subterranean formation with an aqueous solution of said treatment fluid containing a cationic formation control additive for controlling one or both of swelling and sloughing of the formation and potassium formate.
2. Method of claim 1 wherein said potassium formate is present in said aqueous solution in a ratio of 25:75 to 75:25 by weight to said cationic formation control additive in a total concentration in said treatment fluid of at least 0.001% by weight.
3. Method of claim 1 wherein said cationic formation control additive is a polymer of dimethyl diallyl ammonium chloride.
4. Method of claim 1 wherein said cationic formation control additive is a homopolymer of dimethyl diallyl ammonium chloride having a molecular weight from about 1000 to about 500,000.
5. Method of claim 1 wherein said potassium formate is generated in situ by the reaction of formic acid and potassium hydroxide or carbonate.
6. Method of claim 1 wherein said formation control additive is a single site amine or quaternary ammonium compound.

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7. Method of claim 1 wherein said formation control additive is an oligocationic.
8. Method of claim 1 wherein said formation control additive is a cationic polymer.
9. An aqueous well drilling fluid comprising a cationic formation control additive for controlling one or both of swelling and sloughing of the formation and potassium formate.
10. A well drilling fluid of claim 9 wherein said cationic formation control additive is a homopolymer of a compound of the formula $(\text{CH}_2=\text{CH CH}_2)_n\text{N}^+(\text{CH}_3)_{(4-n)}\text{X}^-$ where X^- is a halide anion or an anion which does not adversely react with the formation of interest and n is an integer from 1 to 4.
11. A well drilling fluid of claim 9 wherein said cationic formation control additive is a homopolymer of dimethyl diallyl ammonium chloride.
12. A well drilling fluid of claim 9 wherein said cationic formation control additive and said potassium formate are present in a weight ratio of 75:25 to 25:75.
13. A well drilling fluid of claim 9 wherein said cationic formation control additive is a copolymer of dimethyl diallyl ammonium chloride and about 1% to about 65% by weight acrylic acid or hydrolyzed acrylamide.
14. A well drilling fluid of claim 9 wherein said potassium formate is generated in situ from potassium hydroxide and formic acid.

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15. A well drilling fluid of claim 9 wherein said cationic formation control additive is an oligocationic.

16. A well drilling fluid of claim 9 wherein said cationic formation control additive is a single site cationic formation control additive.

17. A well drilling fluid of claim 16 wherein said cationic formation control additive is a compound of the formula $(\text{CH}_2=\text{CHCH}_2)_n\text{N}^+(\text{CH}_3)_{4-n}\text{X}^-$ where X^- is an anion which does not adversely react with the formation or the treatment fluid, and n is an integer from 0 to 4.

18. A well drilling fluid of claim 16 wherein said cationic formation control additive is a compound of the formula $(\text{CH}_2=\text{CHCH}_2)_n\text{N}^+(\text{CH}_3)_{4-n}\text{X}^-$ where X^- is a halide anion, and n is an integer from 0 to 4.

19. A well drilling fluid of claim 16 wherein said cationic formation control additive is tetramethyl ammonium chloride.

20. A well drilling fluid of claim 9 wherein the combined concentration of said formation control additive and said potassium formate is at least 0.001% by weight of said drilling fluid.

21. Method of claim 2 wherein said cationic formation control additive is tetramethyl ammonium chloride.