PROCESS FOR SOIL STABILIZATION

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ABSTRACT

Soil is treated by contacting it with a slurry of high absorbency alkali metal silicate in a non-aqueous fluid and reacting the silicate with an alkali metal acid phosphate or an amide having the formula

$$\text{O}$$

$$\text{R} - \text{C}-\text{NH}_2$$

wherein R is hydrogen, an alkyl group having one to four carbon atoms, an alkoxy group having one to four carbon atoms or $$-\text{CONX}_2$$ wherein X is hydrogen or an alkyl group having one to four carbon atoms in the presence of from 1 to 2.5 moles of water per mole of alkali metal oxide in the silicate.

10 Claims, No Drawings
PROCESS FOR SOIL STABILIZATION

BACKGROUND OF THE INVENTION

Various methods, both chemical and non-chemical, have been employed in an attempt to stabilize the substrate from which oil is produced. Particularly with respect to sand formations, the aim is to stabilize the loose sand in the deposit while maintaining the permeability of the sand to the flow of oil.

In the old gravel pack technique, larger particles of gravel were deposited around the base hole and the sand was allowed to pack around it. The problem with such a solution remained the difficulty in getting the gravel adequately arranged in the base hole and the criticality in determining exactly the proper size of the gravel to be used. If the gravel was too coarse, the sand still escaped into the oil. If the gravel was too fine, the sand packed and a high pressure drop would be set up around the pack.

Many chemical methods for combatting this problem have been proposed, and the process described in U.S. Pat. No. 2,968,572 issued on Jan. 17, 1961 to Cletus E. Peeler is the currently employed technique. While this method can be used to stabilize sand formations, it suffers the disadvantage of yielding an essentially oil impermeable structure.

SUMMARY OF THE INVENTION

It has now been found that unstable soil formations, particularly sand formations, can be stabilized while oil permeability is maintained when the soil is treated with a slurry of highly absorbent, low bulk density, hydrated alkali metal silicate in a non-aqueous fluid and the silicate is reacted while in intimate contact with the formation, with an amide having the structure

\[ O \quad R - C - \text{NH}_2 \]

wherein R is hydrogen, an alkyl group having one to four carbon atoms, an alkoxy group containing one to four carbon atoms or \(-CON_X \) wherein X is hydrogen or an alkyl group having one to four carbon atoms or an alkali metal acid phosphate or a mixture of any of them in the presence of water. If desired, a reactive additive may be used to speed up the insolubilization of the silicate in the soil.

DETAILED DESCRIPTION OF THE INVENTION

The most critical element involved in achieving stability coupled with permeability in accordance with this invention is the unique silicate employed in the form of a slurry in a non-aqueous fluid. Specifically, the alkali metal silicates are spheroidal, amorphous and have a mole ratio of SiO₂ to alkali metal oxide of 1 to 3.75. The silicates of the invention are characterized by a bulk density of less than 0.5 g./cc. and a maximum water content of 30% by weight. They also have a specific nitrogen surface area between 2.5 and 7 m²/g.

The alkali metal silicates include silicates of sodium, potassium, lithium, rubidium, cesium and mixtures thereof. Sodium silicates are preferred.

Any alkali metal silicate having the above characteristics may be used. One such suitable material is made by contacting essentially discrete alkali metal silicate particles with aqueous solutions of hydrogen peroxide, absorbing the peroxide into the alkali metal silicate hydrated structure and heating the silicate to destroy substantially all of the hydrogen peroxide, thereby causing the silicate to swell and form a high surface area aggregated structure having an extremely high absorbency. These types of silicates and the methods by which they are prepared are discussed in detail in U.S. application Ser. No. 425,970 filed Dec. 19, 1973.

It is important that the silicate be in place in the formation to be stabilized before the insolubilization of the silicate takes place via reaction with the acid phosphate or amide. Generally the silicate is pumped into the formation after it is slurried in a non-aqueous fluid. The concentration of the silicate in the slurry is not critical as long as the slurry is sufficiently fluid to be pumped into the soil to be treated. Generally, 10 to 30 and preferably 20 parts by volume of silicate per 100 parts by volume of the non-aqueous fluid are suitable.

Any non-aqueous fluid which is inert to the silicate and the acid phosphate, amide or reactive salt used in the silicate are employed, including a gas, as long as the fluid is a liquid at the temperature, pressure, porosity and other conditions prevailing in the soil to be treated. Generally, suitable materials would include linear, branched, cyclic, aromatic, aliphatic, saturated or unsaturated hydrocarbons and oxygen-containing hydrocarbons such as epoxides, ketones, alcohols and the like or mixtures of any of them, preferably containing 2 to 30 carbon atoms. The non-aqueous fluid should be inert with respect to the silicate, amide, acid phosphate and any reactive additive used. Specific examples of some suitable materials including the crude oil from the well or any other inert petroleum product or cut, petroleum naphtha, hydrocarbons, liquidified petroleum gas, petroleum ether, methanol, benzene, toluene, xylene, diphenyl ether, dibutyl ketone, biphenyl, cyclopentane, hexadecane, cyclohexane, 4-ethyl-5-methyl octane, eicosane and the like and mixtures of any of them, particularly mixtures of benzene, toluene and xylene.

The volume of the silicate that should be used depends on the vertical interval of the formation and the distance out into the formation away from the well that it is desired to treat. Treatment volume depends on factors such as porosity and surface area. Generally, one volume of silicate per volume of pore space is adequate. In some cases, less of the silicate will protect considerably more pore space. Since the characteristics of soils vary, different treatment volumes will be required depending on soil conditions. Generally, however, it is preferred to inject from 1 to 0.15 volume of silicate per pore volume of the soil to be treated.

Any amide having the formula

\[ O \quad R - C - \text{NH}_2 \]

as defined herein or mixtures thereof may be used. Some such suitable amides include, for example, formamide, acetamide, propionamide, butyramide and N-substituted derivatives such as N-methyl formamide, N,N-dimethyl formamide, N-monoo- and diethyl formamide and the like. Formamide is preferred. Any alkali metal acid phosphate may also be used including sodium, potassium, lithium, cesium, rubidium, and the like acid phosphates, acid pyrophosphates and the like.
The amide and/or acid phosphate and silicate can be so proportioned as to provide insolubilization of the silicate within one-half to eight hours at the temperature of the soil, generally from 0°C. to 250°C. Ideally, the amount of amide to be used varies from 0.2 to 1.5, preferably 0.3 to 0.6, acid equivalents derived via hydrolysis of the amide per equivalent of alkali metal oxide in the silicate at the reaction site. If an acid phosphate is used, the same equivalency at the reaction site based on the acid hydrogen content of the phosphate is used. Any excess amount of the amide and/or phosphate may be used to insure that the specified amount of these materials is available at the reaction site to completely react the silicate.

No reactive salt need be employed unless a high degree of initial gel water insolubility is desired. Any amount of the reactive salt may be used but, because the insolubilized structure would be brittle if reactive salt alone were used to insolubilize the silicate, it is preferred that amounts up to a maximum of 80% of equivalency be employed. Thus, from 0 to 80% of the equivalent amount of the reactive salt needed to react completely with the silicate is preferably present at the reaction site. Any salt reactive to insolubilize the silicate may be employed including, for example, sodium aluminate, sodium bicarbonate, ferric chloride, aluminum chloride, cupric sulfate, cupric chloride, zinc chloride, calcium chloride and the like and mixtures thereof.

The amide or acid phosphates or mixtures thereof may be introduced to the silicate after the slurry is pumped into the formation, or they may be slurried in the nonaqueous medium with the silicate. Any acid phosphate or amide such as formamide, which is a liquid at well temperatures and pressures may be added separately. The amide or acid phosphate may also be dissolved in the additional water and pumped to the silicate slurry already in place in the formation. Although the latter mode of introduction is preferred, any desired method may be used to introduce the amide or acid phosphate to the silicate. Because the volume of amide or acid phosphate and water is small, use of this latter method may require the addition of an excess of these agents to assure the presence of the proper amounts at the reaction site, the location of the silicate particles.

The amount of water required at the reaction site is, at most, the stoichiometrically equivalent amount necessary to hydrolyze the silicate to silica and achieve dissociation of the amide or dissolution of the acid phosphate. Overall, from 0.8 to 2.5 moles of water per mole of alkali metal oxide in the silicate at the reaction site is adequate. When an amide is used, from 1 to 2.5 moles of water should be present at the reaction site per mole of alkali metal oxide in the silicate, and preferably 1.8 to 2.2 moles of water are employed. This amount is adequate to hydrolyze the amide and the silicate. When an acid phosphate is used, from 0.8 to 1.2 moles of water should be present at the reaction site per mole of alkali metal oxide in the silicate. Since the acid phosphate does not hydrolyze but merely dissolves in the water, less water is consumed when an acid phosphate is employed.

The water can be added to the silicate in the formation after or with the amide or with the acid phosphate. When an amide is used, the water can also be mixed into the initial silicate slurry. When an acid phosphate is used, the water is preferably used to dissolve the phosphate so that the phosphate can react. In this instance, the water is introduced as a solution of the phosphate. The water may also be added to the nonaqueous slurry of the silicate. If the amide or acid phosphate is also to be added to the slurry of the silicate in a non-aqueous fluid, the precise amounts of the water and the amide or acid phosphate must be employed to allow an adequate time period within which the composition can be pumped into the soil to be treated before reaction starts. If sufficient water is present in the formation, no additional water need be added. If some water is present but it is not sufficient for the reaction of this invention, supplementary portions of water may be added. The source of the water is irrelevant as long as an adequate amount is available to the amide or acid phosphate and silicate.

The invention is further illustrated but is not intended to be limited by the following examples.

EXAMPLE 1

A slurry is constituted as follows: 20 parts by volume (about 4 grams) of a high-absorbency silicate containing 75% Na₂O, 2.4 SiO₂, and 25% water, 1 part by volume formamide (about 1 gram), 1 part by volume water (about 1 gram), 100 parts by volume of a naphtha cut averaging C₂H₆ (about 70 grams). This slurry is pumped at 25°C. into a loose sand formation, to a volume four times the porosity of the sand. The sand acts to filter out and entraps the silicate particles. The silicate is insolubilized in about 8 hours leaving a stable structure still permeable to oil.

EXAMPLE 2

A slurry comprising 20 parts by volume of a high-absorbency silicate, bulk density 0.15 gram per cc. containing about 20% combined water, in 100 volumes methanol is pumped at 25°C. through a porous, loose sand formation, to a level twice that of the porosity of the sand. 20 Volumes of a 70:30 mixture of formamide:water are pumped through the formation. This is an excess quantity used to insure a sufficient quantity of water and formamide at the reaction site. A stable structure is formed within an hour. The formation is permeable to oil.

EXAMPLE 3

The slurry described in Example 1, excluding the water, using the method outlined in Example 1, is pumped at 25°C. into a sand formation already wet with ground water. An assay of the drained sand shows the presence of at least one part of water per 120 parts of slurry. The silicate sets up in about 8 hours as in Example 1.

EXAMPLE 4

The slurry of Example 1 except that it contains 0.5 part by volume of formamide and no water is pumped at 25°C. into a loose sand formation wet with a 5% solution of calcium chloride in water at a volume four times the porosity of the sand. The drained sand contains at least 5 parts by volume of solution per 120 volumes of slurry. Gelation occurs within 4 hours, to leave a stable, oil-permeable formation.

EXAMPLE 5

A slurry comprising 20 parts by volume of the silicate of Example 1, 100 parts by volume of toluene, 0.5 part by volume of formamide, and 1 part by volume of water
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is pumped at 100°C. into a loose sand formation at a volume four times the porosity of the sand. Gelling occurs within an hour, with additional curing occurring during 8 additional hours at this temperature as evidenced by increasing stability. The formation remains permeable to oil.

EXAMPLE 6

A slurry comprising 20 parts by volume of a (1:2.4) high-absorbency potassium silicate, with a bulk density of 0.2 gram per cc. and a water content of 20%, and 100 parts by volume of cyclohexane is pumped into a porous, loose sand formation at 50°C. to the extent of 3 volumes slurry per volume pore opening in the sand. A solution containing 20 parts by weight of sodium acid pyrophosphate per 100 parts by weight of water is pumped at 50°C. through the sand to a level of three-fourths the pore volume of the sand. Silicate is gelled within one hour and develops increased strength through curing over the next 12 hours to yield a stable, oil-permeable structure.

EXAMPLE 7

The slurry described in Example 6 is pumped, at the same volume, into a porous, loose sand formation containing 1.5% by volume ferric chloride per pore volume. The solution of sodium acid pyrophosphate described in Example 6 is pumped through at a level of one-half the pore volume of the sand. The silicate is gelled within one hour and it develops increased strength during the next 6 hours yielding a stable, oil-permeable formation.

EXAMPLE 8

The slurry described in Example 1 except that two parts of dimethylformamide are substituted for the one part formamide, is pumped into a porous sand formation under the same conditions as described in Example 1. The impregnated sand is then subjected in a bomb to a temperature of 200°C., thus simulating conditions at the base of an oil well. The bomb maintains the developed pressure of the water and dimethylformamide so that vapors cannot escape from the sand. The structure becomes stable within 24 hours and remains oil-permeable.

While the invention has been described in considerable detail in the foregoing, it is to be understood that such detail is solely for the purpose of illustration and that variations can be made by those skilled in the art without departing from the spirit and scope of the invention except as set forth in the claims.

What is claimed is:
1. An improved method for treating soil which comprises contacting the soil with a slurry of highly absorbent, low bulk density, hydrated alkali metal silicate in a non-aqueous fluid and reacting an alkali metal acid phosphate or an amide of the formula

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\text{O}
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R-C-NH_2
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wherein R is hydrogen, an alkyl group having one to four carbon atoms, an alkoxy group having one to four carbon atoms, or \(-CONX_2\) wherein X is hydrogen or an alkyl group having one to four carbon atoms and from 0 to 80% of the equivalent amount of a reactive salt with the silicate in the presence of from 0.8 to 2.5 moles of water per mole of alkali metal oxide in the silicate.

2. The method of claim 1 wherein the alkali metal silicate is sodium silicate.

3. The method of claim 1 wherein the silicate has a ratio of silicon dioxide to alkali metal oxide of 1 to 3.75, a bulk density of less than 0.5 g./cc. and a maximum water content of 30%.

4. The method of claim 1 wherein the silicate is reacted with formamide.

5. The method of claim 1 wherein the silicate slurry is pumped into the soil and the acid phosphate or amide, dissolved in the water, is pumped into soil containing the silicate.

6. The method of claim 1 wherein the acid phosphate or amide is slurried with the silicate, pumped into the soil and the water is introduced into the soil containing the acid phosphate or amide and silicate.

7. The method of claim 1 wherein the silicate is reacted with an amide in the presence of 1.8 to 2.2 moles of water per mole of alkali metal oxide in the silicate.

8. The method of claim 1 wherein the silicate is reacted with an acid phosphate in the presence of 0.8 to 1.2 moles of water per mole of alkali metal oxide in the silicate.

9. The method of claim 1 wherein the amide or acid phosphate provides 0.2 to 1.5 acid equivalents per equivalent of alkali metal oxide in the silicate.

10. The method of claim 1 wherein the non-aqueous fluid is a linear, branched, cyclic, aromatic, aliphatic, saturated or unsaturated hydrocarbon or oxygen-containing hydrocarbon having 3 to 20 carbon atoms.

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