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3,330,347

METHOD OF OIL RECOVERY USING
SURFACTANTS FORMED IN SITU

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No Drawing. Continuation of application Ser. No. 709,784, Jan. 20, 1958. This application Oct. 30, 1964, Ser. No. 407,854

16 Claims. (Cl. 166—9)

This application is a continuation of Ser. No. 709,784, and now abandoned, entitled, "Method of Oil Recovery," filed Jan. 20, 1958, by William O. Brown, Claude E. Cooke, Jr., and Patrick H. Monaghan.

This invention relates to recovery of oil from subsurface reservoirs and especially to recovery of oil from depleted reservoirs or non-productive reservoirs.

Production of oil by any of the known reservoir producing techniques as, for example, water drive, gas cap drive, dissolved gas drive, gravity drainage, etc., leaves significant quantities of oil in the reservoir. The most efficient of these displacement mechanisms, whether the mechanism is a primary (naturally occurring) or secondary (rejuvenating) operation, involves displacement of oil by water. However, even this technique leaves from one-tenth to one-third of the total reservoir pore space filled with oil.

When the water attains a certain local saturation during a water drive or flooding operation, the continuous oil filaments break into disjointed segments which are entrapped and held immobile by capillary forces. In the past, surface-active agents or surfactants have been employed to reduce the magnitude of the capillary forces in an attempt to prevent entrapment of the oil or to free the oil after it has been trapped. In certain instances, where the oil is held at least partly by its adhesion to the rock surfaces, surface-active agents also may act as a detergent.

In a waterflood-type displacement the connate water which is originally present in the reservoir is displaced by the floodwater and forms a bank between the displaced oil and the injected water. Because of the formation of this configuration, the connate water, under any injection conditions, is the water which displaces the oil. Therefore, surfactants in any form cannot be used to prevent trapping of the oil and to be effective, must be designed to work on the trapped oil.

Essentially, then, the initial displacement in a waterflooding process in which a surface-active agent has been added to the floodwater is no different from that which would normally occur in a waterflooding operation in which no surface-active agent is used as an additive to the floodwater. The oil is degraded and trapped in the usual manner and the only value that the surface-active agent serves in the floodwater is to aid in freeing this oil after it has been trapped. However, even for the latter action to be effective, the interfacial tension must be extremely low for practical flooding rates or an additional means must be found of supplying energy to aid in the disintegration of the trapped oil.

Economics restrict the quantity of surface-active agent which may be used. Therefore, surface-active agents added to the waterflood externally are effective only a short distance from the water injection well bore because the restricted quantity used is adsorbed onto the rock.

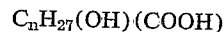
To overcome the above disadvantages in the use of surface-active agents, it has been proposed to form the surface-active agents in situ. Producing surface-active agents in situ has advantages over the simple introduction of surface-active agents to the water used in flooding in that the surface-active agents are produced and con-

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centrated in the interface where they are most needed, and because of this location do not contact the rock surfaces with resultant adsorption by the rock surfaces. Also, variations in the interfacial tension which result from differences in concentration of the surface-active agents at different positions in the interface cause localized stirring and turbulence which tend to cause the trapped oil to emulsify itself spontaneously. Further, the interfacial tension during the transient phase in which a surface-active agent is coming to equilibrium between the oil and water phases may be reduced below its equilibrium value by a factor of 100. This is believed to be the result of the fact that a much larger concentration of surface-active agent is maintained in the interface by in-situ formation than can be attained at equilibrium when the total concentration of surface-active agent is in the water phase.

Various methods which may be utilized for forming the surface-active material in situ are outlined in U.S. application Ser. No. 709,783, filed Jan. 20, 1958, now U.S. Patent No. 3,298,436, entitled, "Method of Oil Recovery," by W. M. McCardell. For example, the surfactants may be formed by the reaction between a basic floodwater and oil-soluble acids. The reactive, oil-soluble material may be introduced into the reservoir in a hydrocarbon oil or the reactive acid material may be indigenous to the oil phase of the reservoir. The hydrocarbon oil may be, e.g., reservoir oil from the same reservoir into which the acid material is introduced or reservoir oil from a different reservoir. In either case, the reactive material is first mixed at the surface with reservoir oil and, then, this mixture is injected into the reservoir to be waterflooded.

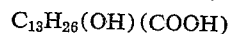
Suitable oil-soluble acids that may be used are organic acids such as saturated aliphatic acids of the general formula, $C_nH_{2n+1}COOH$ as, for example, lauric acid, $C_{11}H_{23}COOH$, myristic acid, $C_{13}H_{27}COOH$, palmitic acid, $C_{15}H_{31}COOH$, stearic acid, $C_{17}H_{35}COOH$, monoethylenic aliphatic acids of the general formula, $C_nH_{2n-1}COOH$ as, for example, lauroleic acid, $C_{11}H_{21}COOH$, myristoleic acid, $C_{13}H_{25}COOH$, palmitoleic acid, $C_{15}H_{29}COOH$, oleic acid, $C_{17}H_{33}COOH$; dienolic aliphatic acids of the general formula $C_nH_{2n-3}COOH$ as, for example, linolenic acid, $C_{17}H_{31}COOH$, 9, 11 octadecadienoic acid, $C_{17}H_{31}COOH$; trienoic aliphatic acids of the general formula, $C_nH_{2n-5}COOH$, as, for example, linolenic acid $C_{17}H_{29}COOH$, eleostearic acid, $C_{17}H_{29}COOH$; hydroxy aliphatic acids of the general formula,



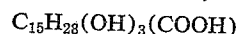
as, for example, hydroxylauric acid,



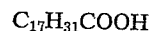
sabinoic acid, $C_{11}H_{22}(OH)(COOH)$ hydroxymyristic,



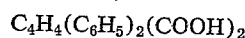
hydroxypalmitic, $C_{15}H_{30}(OH)(COOH)$, hydroxystearic, $C_{17}H_{34}(OH)(COOH)$, aleuritic acid,



ethylenic hydroxy aliphatic acids of the general formula, $C_nH_{2n-2}(OH)(COOH)$ as, for example, ricinoleic acid, $C_{17}H_{32}(OH)(COOH)$; cyclic acids, as, for example, hydnocarpic acid, $C_{15}H_{27}COOH$, chaulmoogric acid,



halogenated aliphatic acids of the first four classes or aliphatic acids; dicarboxylic acids as, for example, azelaic acid, $C_7H_{14}(COOH)_2$; and aromatic acids as, for example, truxillic acid and its isomer, truxinic acid,



chlorogenic acid $C_8H_8(OH)_5(COO)(COOH)$, abietic acid, $C_{18}H_{20}(COOH)_2$.

It has been discovered that the presence of bivalent cations, especially Ca^{++} and Mg^{++} , have an adverse effect upon the ability of surface-active agents formed in situ to lower the interfacial tension. Although the interfacial tension may be reduced by formation of the surface-active agents in situ, it is not reduced as low as possible if few or no bivalent cations are present.

Since almost all water (subsurface salt water) available in secondary recovery waterflooding projects contains significant amounts of bivalent cations, especially Ca^{++} and Mg^{++} , it is desirous to overcome the adverse effect they have on lowering of the interfacial tension.

The bivalent cations present in subsurface water may be rendered ineffective by adding a chelating agent, such as the sodium salts of ethylene diamine tetraacetic acid. Addition of the chelating agent forms an organic or other complex with the bivalent cations which is water soluble and will not ionize. For example, when a basic water is treated with a chelating agent and is brought into contact with an oil containing an acid, the surfactants produced at the oil-water interface will cause a lowering of the interfacial tension substantially below that which would be obtained with untreated water.

The bivalent cations present in subsurface water also may be rendered ineffective by chemical means as by adding sodium carbonate, sodium bicarbonate, or carbon dioxide to the floodwater in an amount sufficient to reduce the cation concentration in the floodwater to not more than 10^{-5} mols per liter.

Therefore, it is an object of this invention to provide a method wherein the detrimental effect of bivalent cations in waterflooding operations utilizing the formation of surface-active agents in situ is lessened or eliminated.

Briefly, the invention comprises a method for increasing oil recovery from underground reservoirs comprising the steps of injecting water containing material for producing surface-active agents in situ into a sub-surface reservoir, the water being treated to reduce the bivalent cation concentration thereof.

The data in Table I show the reduction in interfacial tension by use of chelating agents. These data were obtained in the laboratory by the methods described by (1) Hauser et al., J. Phys. Chem., 42, 1001, 1938, and (2) A. S. Michaels, M.S. Thesis, MIT, 1947.

TABLE I.—INTERFACIAL TENSIONS MEASURED BY PENDANT DROP APPARATUS BETWEEN FORMATION WATER AND CRUDE FROM COLORADO FIELD, JIM HOGG COUNTY

pH	Chelating Agent	Interfacial Tension, dynes/cm.
7.2	None	36.0
9.5	do	20.0
9.5	Disodium dihydrogen ethylene diamine tetraacetate.	0.10
9.5	Tetrasodium ethylene diamine tetraacetate.	0.20

Table I shows substantial reduction of the interfacial tension by the addition of a chelating agent. The interfacial tension decreased from 36 to 20 dynes/cm. upon an increase of pH from 7.2 to 9.5. However, at pH of 9.5 where the interfacial tension is 20 dynes/cm. the interfacial tension dropped to 0.10 dynes/cm. by the addition of the chelating agent disodium dihydrogen ethylene diamine tetraacetate. Similarly, at pH of 9.5, the interfacial tension dropped from 20 dynes/cm. to 0.20 dynes/cm. by the addition of the chelating agent tetrasodium ethylene diamine tetraacetate.

The alternative chemical method concerns removal of the cations. At pH of 8.5 calcium carbonate has a solubility product of 10^{-9} mols per liter. For effective forma-

tion of surface-active agents in situ, a cation concentration of not more than 10^{-5} and more preferably 10^{-6} mols per liter is desired. To attain a cation concentration of 10^{-5} – 10^{-6} mols per liter at pH of 8.5 when the solubility product is 10^{-9} mols per liter, the carbonate ion must be present in concentration of at least 10^{-3} mols per liter. The carbonate ion may be introduced as sodium carbonate, sodium bicarbonate, or carbon dioxide.

To illustrate this method formation water and oil from the Colorado field was tested at pH of 9.5. The interfacial tension was found to be 20 dynes/cm. Analysis of the water showed the cations (calcium and magnesium) were present in concentrations of 528 p.p.m. as chlorides and bicarbonates, 338 p.p.m. as bicarbonates. Sodium carbonate then was added to produce a carbonate concentration of 10^{-3} mols per liter. Calcium and magnesium act very similarly in this method. With the carbonate ion present in a concentration of 10^{-3} mols per liter the calcium and magnesium ion is reduced to 10^{-6} mols per liter. It required 2.67 grams of sodium carbonate per liter of water, 0.935 lb. of sodium carbonate per barrel of water. After this treatment the interfacial tension was 0.12 dyne/cm. at pH of 8.5.

Having fully described the nature, objects and method of the invention, we claim:

1. In a waterflood displacement process for increasing oil recovery from an underground reservoir penetrated by spaced-apart water injection and oil-production wells in which reactive, oil-soluble organic acid material in the oil phase of the reservoir and reactive, water-soluble basic material in the injected floodwater react to produce surface-active material at the oil-water interface, the improvement comprising treating said floodwater prior to injection thereof into said reservoir to reduce the bivalent cation concentration thereof.

2. A method as recited in claim 1 in which treating said floodwater comprises adding a chelating agent to the water to form a water-soluble nonionizing complex with the bivalent cations in the water.

3. A method as recited in claim 2 in which the chelating agent comprises disodium dihydrogen ethylene diamine tetraacetate.

4. A method as recited in claim 2 in which said chelating agent comprises tetrasodium ethylene diamine tetraacetate.

5. A method as recited in claim 2 in which treating said floodwater comprises treating the water with carbonate ion to reduce the bivalent cation concentration thereof.

6. A method as recited in claim 5 in which the bivalent cation concentration is reduced to not more than 10^{-5} mols per liter.

7. A method as recited in claim 5 in which the carbonate ion is introduced as sodium carbonate.

8. The method of recovering petroleum oil from natural reservoirs comprising injecting through an injection well into the oil-containing formation a solution of a first reactant in a hydrocarbon solvent miscible with the oil in said reservoir, treating an aqueous solution of a second reactant to reduce the bivalent cation concentration of said aqueous solution, thereafter injecting into the reservoir said treated aqueous solution, said second reactant being capable of reacting with said first reactant under reservoir conditions to form a surfactant, thereafter injecting water into the reservoir in sufficient quantity to produce oil from said reservoir.

9. A method as recited in claim 8 wherein treatment of said aqueous solution comprises adding a chelating agent to said aqueous solution to form a water-soluble, nonionizing complex with the bivalent cations in said aqueous solution.

10. A method as recited in claim 9 in which the chelating agent comprises disodium dihydrogen ethylene diamine tetraacetate.

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11. A method as recited in claim 9 in which said chelating agent comprises tetrasodium ethylene diamine tetraacetate.

12. A method as recited in claim 8 in which treatment of said aqueous solution comprises adding carbonate ion to said aqueous solution. 5

13. A method as recited in claim 12 in which the bivalent cation concentration is reduced to not more than 10^{-5} mols per liter.

14. A method as recited in claim 12 in which the carbonate ion is introduced as sodium carbonate. 10

15. A method as recited in claim 8 in which said hydrocarbon solvent is reservoir oil.

16. A method as recited in claim 8 in which said hydrocarbon solvent is said formation oil. 15

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