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METHOD FOR RECOVERY OF PETROLEUM OIL FROM CONFINING STRUCTURES

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ABSTRACT OF THE DISCLOSURE

A method is provided for enhancing the movement of a heavy crude petroleum oil through a confining structure such as a reservoir. Ammonia is introduced into the petroleum oil while the oil is in the presence of water, to form ammonium soaps. The ammonium soaps cause the formation of an oil-in-water emulsion having a viscosity lower than that of the oil. A driving fluid is introduced to cause the emulsion and associated crude to move through the confining structure. In one embodiment, decomposition of the ammonium soaps and the formation of other soaps is accomplished by the introduction of thermal energy, so that the area of lowered viscosity is effectively increased.

BACKGROUND OF THE INVENTION

This invention relates to the art of enhancing the movement of petroleum oils, and particularly heavy crude oils, in the context of secondary recovery operations, for example.

The inherent nature of heavy crude petroleum oils is such that it is difficult to accomplish movement of the oil through a confining structure, particularly when the confining structure is the earth formation in which the crude occurs as a natural deposit. Even when the crude petroleum oil is heavy, the native energy available in the formation, arising from natural water or gas pressure, is sometimes adequate to allow recovery of a substantial portion of the crude by primary recovery techniques. Secondary recovery of heavy crude oils is difficult, however, and even the highly developed steam stimulation, water flood, gas drive, and miscible fluid displacement techniques have failed to solve secondary recovery problems in many cases. Such problems arise to a considerable degree from the high viscosity of the crude petroleum oil, and are therefore encountered in operations other than secondary recovery, though secondary recovery represents perhaps the most commercially significant area of difficulty.

The economics of heavy oil production are adversely affected not only by the high costs of secondary recovery but also by the fact that these crudes when produced are more expensive to transport and require more (and consequently more expensive) processing to the final product than do the lighter petroleum oils. The price of heavy crude at the wellhead is thus lower than the price of lighter oils. More efficient means of production are necessary today to make the heavy oils competitive in price with the lighter oils.

It is forecast that in the near future, heavy oils will become the primary source of petroleum. Thus, the viability of the petroleum industry will depend upon the ability to produce these oils at low cost.

These facts combine to create a continuing need for improvement in technology in this field.

SUMMARY OF THE INVENTION

In summary, the invention provides a method for enhancing the movement of crude petroleum oil in a confining structure, especially advantageous for use with

heavy crude, which comprises introducing ammonia into the confining structure in such fashion that the ammonia contacts the crude while the oil and ammonia are in the presence of water. The ammonia spontaneously reacts with the acid content of the petroleum oil to produce a significant yield of ammonium soaps, in situ, and the ammonium soaps thus formed cause at least some of the oil and water to form an oil-in-water emulsion. This emulsion has a viscosity which is markedly lower than that of the petroleum crude, and thus is significantly more free flowing.

A driving fluid may then be introduced to cause movement of the emulsion and the petroleum oil associated therewith through the confining structure. As will be explained more fully below, special benefits are realized by the use of certain driving fluids such as steam.

DESCRIPTION OF PREFERRED EMBODIMENTS

The invention provides a method whereby the movement of petroleum oils within a confining structure, particularly an earth formation, is markedly enhanced without the necessity for employing complicated manipulative procedures or unduly expensive chemical additives.

Broadly considered, the invention is based on the reaction of ammonia with native constituents of the petroleum oil to yield products in situ which cause at least some of the petroleum oil to form an oil-in-water emulsion of markedly lower viscosity than the petroleum oil itself, the decreased viscosity of the emulsion being utilized to obtain freer movement of the petroleum oil. The invention can be practiced with particular advantage in the secondary recovery of heavy petroleum crude oils having a relatively high content of native organic acids, and is especially useful when the crude has an acid number of at least 3. When employing the invention for secondary recovery of crude petroleum oil, any of the known secondary recovery techniques can be adopted which are aided by a significant reduction in viscosity of the crude oil, such techniques including thermal stimulation, water flooding, gas drive, and miscible fluid displacement, the particular technique employed depending upon the specific nature of the oil deposit involved.

The ammonia may be introduced in liquid form, either as liquified anhydrous ammonia or as an aqueous ammonium hydroxide solution, or it may be introduced in gaseous form as ammonia vapor. Thus, in secondary oil recovery from a formation not subject to excessive fingering or channelling, ammonia can be introduced via an injection well and followed with a driving fluid, e.g., water or steam, to force the ammonia and resulting oil-in-water emulsion through the formation toward an outlet or recovery well. In cases where thermal stimulation is feasible, the ammonia can be introduced via an existing well, followed by introduction of the steam, oil then being produced via the same well, as by pumping. In other cases, particularly where the formation is suitable for water flooding, the formation can be flooded with an aqueous solution of ammonium hydroxide, with the concentration of ammonia as low as 0.5% by weight.

The invention is particularly effective when the ammonia introduced into the formation or other confining structure is followed by steam or other thermal energy source at temperatures adequate to effect thermal decomposition of a portion of the ammonium soaps produced by reaction of the ammonia with the acid content of the petroleum oil. Under such circumstances, the ammonium soaps first produced cause a portion of the petroleum oil to form an oil-in-water emulsion, with this emulsion appearing as a bank or barrier in advance of the steam or other hot fluid. The effect of the thermal energy supplied by the steam or the like is then to thermally decompose a portion of the ammonium soaps in the emulsion, yield-

ing free ammonia which comes into contact with additional petroleum oil in advance of the emulsion, so that this ammonia again reacts with the native acids of the petroleum oil to form fresh ammonium soaps which in turn cause a part of the oil in this new location to form an oil-in-water emulsion. Thus, in effect, the steam or other heat source serves to create what can be characterized as an advancing emulsion barrier which in turn is a source of ammonia for emulsification of additional petroleum oil as the barrier advances through the formation.

Since success of the invention depends upon the decrease in viscosity resulting from formation of an oil-in-water emulsion, presence of water is of course essential. In secondary recovery of oil, the water is conveniently present as a native constituent of the formation, and the invention can thus be practiced with completely anhydrous ammonia. When water is not present in the confining structure, or is present in an amount insufficient to form the desired oil-in-water emulsion, the ammonia can then be introduced conveniently as an aqueous ammonium hydroxide solution.

In all embodiments of the invention, the ultimate effect of the oil-in-water emulsion is to bring about what amounts to an overall reduction in viscosity of a relatively large amount of crude oil in addition to that which is present in the emulsion. Thus, when the invention is employed in a secondary recovery procedure which utilizes heat, as from steam, to render the oil less viscous, the oil-in-water emulsion resulting from the presence of the in-situ-formed ammonium soaps serves to render a substantially larger quantity of oil recoverable as a result of the supplied heat. Similarly, presence of the oil-in-water emulsion provides a more extensive oil-moving effect when a drive fluid is used.

Though, in theory, other bases than ammonia would seem suitable for reaction with native acids of crude petroleum oil according to the invention, ammonia has proved markedly superior for several reasons. First, and of particular importance, the ammonium soaps are very highly water soluble, distinctly more so than sodium soaps, for example, so that the desired oil-in-water emulsions, are obtained more effectively, and in greater yield, when ammonia is used. Also, the ammonium soaps show less tendency to plate out on formation clays and the like, and are thus less wasteful, then is true for sodium and like soaps. Then, the thermal instability of the ammonium soaps promotes regeneration of ammonia when heat is supplied to the emulsion bank, as by steam, so that the ammonium soaps provide for an inherent extension of the emulsion bank over a larger area in the formation. Finally, the cost of ammonia is sufficiently low, in view of its marked effectiveness, to make use of this agent feasible as an additive in secondary recovery operations.

EXAMPLE I

A laboratory test was performed using a sample of crude petroleum oil from the Toborg Field in West Texas. This sample was of high specific gravity and of high native acid content, exhibiting an acid number in excess of 5.

A pyrex glass tube, two feet long and three inches in diameter, was packed with 20–30 mesh Ottawa sand. The sand was introduced with a sand distributor and vibrated with a rubber mallet. The packed tube was weighed, filled with a water under vacuum, and reweighed. The tube was oriented in the vertical position.

The pore volume was calculated from the volume of water in the tube. The water was displaced by oil from the top of the tube downward. After filling with oil, the displaced water was weighed and again the volume was calculated to determine the volume of oil in the sand pack. Fluid injection was controlled with a Grove constant nitrogen pressure regulator and Moore Products' low-flow controller with a metering valve.

Approximately 1.2 pore volumes (120% pore volume) of water were introduced into the tube, and the water/oil ratio was then about 20. 50 cc. (5.46% pore volume) of 1 N ammonium hydroxide was then injected into the tube, and the system was allowed to stand for 18 hours to effect emulsification. Water was then again injected until the ratio of water/oil was greater than 19. The total oil and water injected equal about 2.25 (225%) pore volumes.

Oil was continuously produced from the tube during the injections, except for shut-downs at the following times:

50 minutes after about 53% pore volume injected
25 minutes after the ammonium hydroxide injection
90 hours after about 125% pore volume injected
74 hours after about 192% pore volume injected

The percentage of oil recovered from the tube showed a marked and steady increase during the introduction of the first 0.65 pore volume of water. At this point, approximately 42% of the oil had been recovered. Recovery then began to taper off rapidly, and just before the ammonium hydroxide injection (at 120% pore volume) about 49% of the oil had been recovered.

Following introduction of the ammonium hydroxide, production began to show a marked increase as illustrated by the following recoveries as compared to the pore volume injected:

Percent pore volume:	Percent recovery
140	58
150	64
160	68

Production then began to slightly taper off, and at the end of introduction of 200% pore volume, 80% recovery was noted. At 225% pore volume, the recovery was approximately 84%.

As a result of the injection of ammonium hydroxide and the continued injection of water, the recovery of the oil was increased by 71.07% (34.38% of the original oil).

EXAMPLE II

Example I was repeated using a Tulare zone crude petroleum oil from the North Midway field in California. This sample was also of high specific gravity and high native acid content. The acid number was in excess of 5.

Approximately 2.25 pore volumes of water were first injected, and this injection was followed by an injunction of 5.71% pore volume of 17 N ammonium hydroxide. Further water was then injected until the total water and NH_4OH injection was about 342% pore volume.

Oil was continuously produced from the tube during the injections, except for shut-downs at the following times:

17 hours after about 116% pore volume
50 minutes after about 212% pore volume
65 hours after the NH_4OH injection

The oil recovery had been steadily but slowly increasing before the ammonium hydroxide injection, from about 51% recovery at about 132% pore volume, to about 65% recovery at the NH_4OH injection (225% pore volume).

Following injection of the ammonium hydroxide, the recovery began to exhibit a sharp increase, going from about 68% at 224% pore volume, to 80% at 270% pore volume. At about 332% pore volume, 90% of the oil had been recovered.

Injection of the ammonium hydroxide followed by continued water injection resulted in recovery of 25.59% more of the total oil. 90.76% of the total oil was produced.

EXAMPLE III

A steam stimulation test was performed to determine the effect of ammonia injection followed by steam injection on the secondary recovery of oil from the Tulare

zone in California. The Tulare zone crude was found to have a high native organic acid content, with an acid number in excess of 5.

Through a well which had previously been drilled into the producing formation, about 25 barrels of lease crude oil was injected at 5 bbl./min. and 25 p.s.i.g.

Ninety barrels of liquid ammonia at 30° F. and 100 p.s.i.g. was then injected at the rate of about 3 bbl./min. This step was followed by a further injection of 70 barrels of lease crude, at 5 bbl./min. and 25 p.s.i.g.

Steam was then injected into the well at a rate of 450 bbl./day until 1,470 barrels had been injected. Steam conditions at the wellhead were 250–275° F. and185–200 p.s.i.g.

All injections were made into the annulus between casing and tubing. During the initial period of injection, the tubing was left open until clear of oil, it was then closed at the surface.

For the two-month period immediately preceding the ammonia injection, the well had produced no more than 12 bbl./day. An injection of 499 barrels of steam about three weeks before the ammonia injection had resulted in no significant increase in production rate.

A short time after the ammonia-steam injections, however, the production through the well began to increase markedly, and about three weeks after such injections had reached a peak of about 35 bbl./day.

The foregoing examples are illustrative embodiments of the invention and should not be construed as limiting.

For instance, in Example III above, about 25 barrels of lease crude were injected into the well before the ammonia injection. This was done as a safety measure (to prevent a reaction of the ammonia in the well bore) and is not thought to be necessary.

It is contemplated that the ratio by volume of introduced ammonia to introduced steam will be less than about one to ten. In fact, it will often be desired to use a ratio of about one to twenty or less. It will be readily understood that any process which requires the use of too much ammonia (or any other chemical, even those which are commonly considered inexpensive) will be economically unfeasible, and hence inoperable for practical purposes.

It is further contemplated that, where steam is employed, the steam will be introduced at about 250–500° F., and about 150–200 p.s.i.g.

While the invention has been described in terms of specific examples, it will be understood by those skilled in the art that various changes and modifications may be made in the examples illustrated without departing from the scope of the invention, which is defined by the following claims.

What is claimed is:

1. The method for enhancing movement of crude petroleum oil through a confining structure when the oil has a significant native acid content, comprising:
   - introducing ammonia into the confining structure in such fashion that the ammonia contacts the petroleum oil while the oil and the introduced ammonia are in the presence of water,
     - said ammonia reacting spontaneously with the native acid content of the petroleum oil to produce a significant yield of ammonium soaps in situ,
     - said ammonium soaps causing at least some of the petroleum oil and said water to form an oil-in-water emulsion of markedly lower viscosity than the petroleum oil; and
   - introducing a driving fluid into the confining structure to cause petroleum oil to move therethrough with said emulsion causing freer movement of the petroleum oil because of the lower viscosity of the emulsion.

2. A method according to claim 1, wherein said ammonia is introduced in the form of an aqueous ammonium hydroxide solution.

3. A method according to claim 1, wherein
   - the confining structure is an oil-bearing earth formation, and
   - said ammonia and said driving fluid are introduced via an injection well.

4. A method according to claim 1, wherein
   - said driving fluid is steam,
     - said steam being introduced at a temperature such as to both reduce the viscosity of the petroleum oil and thermally decompose at least some of said soaps to produce ammonia as a product of the decomposition,
     - the ammonia so produced proceeding in advance of the steam drive so as to come in contact with fresh petroleum oil and react with the native acid content thereof to again produce a significant yield of ammonium soaps in situ, the soaps so produced causing at least some of the petroleum oil to form an oil-in-water emulsion, whereby freer movement of the petroleum oil is realized over a greater area.

5. A method according to claim 4, wherein the ratio by volume of introduced ammonia to introduced steam is less than about one to ten.

6. A method according to claim 4, wherein said steam is introduced at about 250–500° F. and about 150–200 p.s.i.g.

7. A method according to claim 1, wherein said ammonia is introduced at least about 30° F. and at least about 100 p.s.i.g.

8. A method according to claim 1, wherein the acid number of the petroleum oil is at least about 3.

9. The method for enhancing movement of crude petroleum oil having a significant native acid content through a producing oil reservoir comprising
   - introducing crude oil into the producing oil reservoir through an injection well, to sweep interstitial water away from the well;
   - introducing ammonia into the reservoir through said injection well, in such fashion that the ammonia contacts the petroleum oil while the oil and the introduced ammonia are in the presence of water;
     - said ammonia reacting spontaneously with the native acid content of the petroleum oil to produce a significant yield of ammonium soaps, in situ,
     - said ammonium soaps causing at least some of the petroleum oil and said water to form an oil-in-water emulsion of marked lower viscosity than the petroleum oil; and
   - introducing a driving fluid into the reservoir to cause petroleum oil to move therethrough with said emulsion causing freer movement of the petroleum oil because of the lower viscosity of the emulsion.

10. A method in accordance with claim 9, wherein a slug of crude oil is introduced after the introduction of ammonia and before the introduction of said driving fluid.

11. The method for increasing the recovery of crude petroleum oil from an oil producing reservoir comprising
   - introducing ammonia into said oil producing reservoir in such fashion that the ammonia contacts the petroleum oil while the oil and the introduced ammonia are in the presence of water,
     - said ammonia reacting spontaneously with the native acid content of the petroleum oil to produce a significant yield of ammonium soaps in situ,
     - said ammonium soaps causing at least some of the petroleum oil and said water to form an oil-in-water emulsion of markedly lower viscosity than the petroleum oil;
   - introducing steam into said oil producing reservoir at a temperature such as to both reduce the viscosity of the petroleum oil and thermally decompose at least some of said soaps to produce ammonia as a product of the decomposition, said ammonia being

effective to react with the native acid content of other oil to form further ammonium soaps in situ, the soaps thus produced being effective to form further oil-in-water emulsion, whereby freer movement of the petroleum oil is realized over a greater area.

12. The method for increasing the recovery of crude petroleum oil from an oil producing reservoir comprising

introducing ammonia into said oil producing reservoir through a well communicating to said reservoir from the earth's surface, in such fashion that the ammonia contacts the petroleum oil while the oil and the introduced ammonia are in the presence of water,

said ammonia reacting spontaneously with the native acid content of the petroleum oil to produce a significant yield of ammonium soaps in situ,

said ammonium soaps causing at least some of the petroleum oil and said water to form an oil-in-water emulsion of markedly lower viscosity than the petroleum oil;

introducing steam into said oil producing reservoir at a temperature such as to both reduce the viscosity of the petroleum oil and thermally decompose at least some of said soaps to produce ammonia as a product of the decomposition, said ammonia being effective

to react with the native acid content of other oil to form further ammonium soaps in situ, the soaps thus produced being effective to form further oil-in-water emulsion, whereby freer movement of the petroleum oil is realized over a greater area; and,

causing movement of said emulsion and accompanying crude petroleum oil to said well to produce said fluids, thereby effectively increasing the recovery of crude oil from the well.

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