

[54] METHOD FOR RECOVERY OF OIL

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3,490,532	1/1970	Carlin	166/272 X
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[52] U.S. Cl. 166/272

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[58] Field of Search 166/270, 272, 271, 268,
166/274, 275, 303

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[57]

ABSTRACT

A steam displacement process is provided for the post-primary recovery of petroleum oil, which includes adding very small amounts of caustic material such as sodium hydroxide to the steam which is used in the displacement process.

15 Claims, No Drawings

[56]

References Cited

UNITED STATES PATENTS

3,279,538	10/1966	Doscher	166/272 X
3,464,492	9/1969	Friedman	166/272 X
3,476,183	11/1969	Haynes, Jr. et al.	166/272

METHOD FOR RECOVERY OF OIL

BACKGROUND OF THE INVENTION

This invention relates to methods for recovery of subterranean mineral deposits, especially oil, in connection with steam flooding techniques. The use of the methods provided by the invention will increase the percentage of oil recovered in many post-primary recovery processes.

Post-primary processes are used to recover oil which remains in subterranean formations after initial recovery methods have been completed. Several general types of such processes are employed, one commonly-used type of process being generally referred to as "steam flooding." The present invention relates to this type of process.

While many different variations of steam flooding processes are either in use or have been proposed, improvement in the known processes, particularly with respect to the cost of the methods and the percentage of oil recovered, seems to always be possible. Especially because of the great value of the oil and the great cost of such methods, improved methods are constantly sought by the industry at great exchange of research and development dollars.

The present invention provides such an improved process, which utilizes injection of small amounts of a caustic material in conjunction with a steam flooding operation, and which in many contexts of use will provide for increased efficiency of recovery of oil at reasonable cost.

There have been many prior art efforts to increase recovery through post-primary processes, and many of these efforts—represented by hundreds of prior patents and literature disclosures—have been directed to the steam flooding type of post-primary process.

Some processes have been proposed which involve use of alkaline materials, such as sodium hydroxide or other alkali metal hydroxide.

One of the prior art methods which is pertinent to the present invention is represented by the patent to Doscher, U.S. Pat. No. 3,279,538. Doscher's objectives and working environment are quite unlike those of this invention, but there are similarities in the processes employed. Doscher's use of alkali metal hydroxide materials, however, is in connection with a process which includes fracturing the formation between injection and producing wells [the formation is not fractured in this invention], leaching tar sands and forming an oil-aqueous emulsion, neither of which are desired by applicant in this invention.

There have been many other prior efforts to improve oil recovery, and a number of suggestions have been made which have found considerable utility in certain contexts of use. The present invention, however, provides for at least those contexts of use in which its utility has been investigated to date, the most economical and efficient means of increasing the rate and percentage of oil recovery yet known to applicant.

SUMMARY OF THE INVENTION

In its broadest terms, the invention relates to methods for recovery of oil which comprise adding very small amounts of an alkali metal hydroxide to the liquid phase of wet steam, and then utilizing such steam in flooding areas of the oil-containing reservoir.

In one embodiment, the injection of steam without hydroxide solution is continued for an extended period of time after injection of the hydroxide solution has been terminated.

In another embodiment, the hydroxide solution is injected in increasingly more dilute concentrations as the injection proceeds.

In yet another embodiment, the hydroxide solution is injected intermittently with steam which is continuously injected.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The description which follows is of the embodiments of the invention which applicant considers the preferred embodiments and best mode of the invention at the time of this application.

It is customary in post-primary recovery processes, such as secondary and tertiary recovery, to utilize at least one injection well communicating with a subterranean oil-producing formation, and at least one producing well communicating with the same formation. Generally, a plurality of both injection wells and producing well is employed.

In such processes, it is customary to inject fluids, such as water or steam, through the injection well or wells, and produce well fluids from the producing well or wells. Sometimes, such processes are economically feasible even if the incremental increase in production is very small. Of course, it is always desired to increase the percentage recovery of oil as much as possible. That desire must be weighed against the cost of the particular post-primary recovery process employed.

This invention is concerned with the steam flooding type of post-primary recovery process. It has been found experimentally that upon completion of a steam flooding project, on the order of about 30 percent of the pore volume of a typical formation is generally occupied by steam vapor, the balance of the pore volume of the formation being occupied by liquid phase, water (hot and cold) and oil.

The drainage efficiency of those areas which are occupied by steam vapor is much greater than for those areas occupied by the liquid phase; the present invention is directed to improving the speed and efficiency of recovery of oil from the latter areas of the formation.

In accordance with the invention, steam is provided for injecting into an injection well, the steam being either "dry" steam, i.e., substantially 100 percent vapor, or "wet" steam, i.e., having both vapor and liquid phases.

An alkali metal hydroxide material is mixed for use in very small concentrations with the steam, either by forming a solution in the liquid phase of wet steam, or by providing a separate aqueous solution for use with dry steam.

Applicant prefers to use, as the alkali metal hydroxide sodium hydroxide. Potassium hydroxide is also useful, although applicant believes that it is not as satisfactory in most contexts of use as sodium hydroxide.

The steam and hydroxide solution are injected into the formation through the injection well or wells, thereby heating the formation. Upon injection into the formation, the hydroxide reacts with the organic materials present in the connate water of the heated formation, to form in situ surface active agents. The term

"connate" water as used in this application includes not only water trapped in the formation, but also water moving therethrough.

The exact reactions which occur in the formation are not known to applicant at the time of this application. Nor does applicant fully appreciate the nature of the reactants in the connate water. Since the nature and content of the connate water vary from formation to formation, both the nature of the reactants and the nature of the reaction would be expected to differ, perhaps radically, from formation to formation.

As would be expected, therefore, the present invention is more advantageously employed in some formations than in others.

Applicant has tested the methods of the invention, in laboratory tests constructed to simulate field conditions. These tests, which form the basis of the examples given later in this specification, reveal that for the samples tested (from the Kern River area of California), significant improvement in oil recovery is realized.

While the focus of the above discussion has been on reaction of the hydroxide material with the connate water, applicant has noted as well some reaction of the hydroxide with organic compounds in the boiler feed water. The nature of the reaction products formed, again dependent on the nature of the water, are believed to be roughly comparable with those formed in the connate water. Any such surface active agents formed with the boiler feed water are supplemental to, and not in lieu of, those formed with the connate water of the formation.

The surface active agents thus formed in situ (and perhaps in the feed water, are effective to reduce the interfacial tension between the oil and water in the formation. Reduction of such interfacial tension is effective to facilitate removal of the oil by greatly improving drainage in those regions of the formation occupied by the liquid phase.

Intimate contact of the surfactants thus formed with as much of the liquid-occupied portion of the formation as possible, is desired. Such contact is assured by driving the hydroxide-containing material further into the formation. This may be conveniently and more economically done by providing additional steam not having hydroxide material added thereto, which is injected through the injection well or wells after injection of the hydroxide-containing material has been terminated. In accordance with this preferred embodiment of the invention, injection of the steam sans hydroxide is continued for a period of time equal to at least about one-half the period of time during which hydroxide-containing steam was injected. For best results it is believed that the ratio of the time period of injection of hydroxideless steam to the time period of injection of hydroxide-containing steam, should desirably be no greater than one. Thus, the hydroxide injection stage would continue over a period of from about one-half to about two-thirds of the life of the injection project.

Alternatively, the pH of the water produced at the producing well may be monitored, and the hydroxide injection may be desirably discontinued when a significant increase in such pH is noted.

The concentration of the hydroxide in the injected solution is desirably quite small. Applicant believes that the concentration of the preferred sodium hydroxide should not exceed about 0.5 percent and for best results should be in the range of 0.05 to 0.1 percent, all

percentages specified in this application being by weight. Applicant further believes that the concentration of sodium hydroxide should be at least about 0.025 percent in order to provide for the formation of an adequate amount of surface active agents to significantly improve the efficiency of oil recovery.

Similar concentrations should be employed in the event potassium hydroxide is employed.

These percentages are important to best results using the invention. At concentrations less than those preferred, insufficient improvement in recovery is realized. At concentrations greater than those specified, in addition to the increased costs resulting, it has been found surprisingly that, again, insufficient improvement is realized. Further, at higher percentages; undesirable oil-water emulsions are formed which are difficult to break.

In accordance with one desirable embodiment of the invention, the concentration of hydroxide material is reduced following its initial injection, so that the concentration of hydroxide material in the initial injection is greater than the concentration in the final injection. The decrease in concentration may be gradual, on a continuous feed basis, or it may be stepped as in a batch operation, in any suitable number of steps.

A decrease in sodium hydroxide concentration, for example, from at least about 0.1 percent, and perhaps as much as about 0.5 percent, to a concentration no greater than about 0.025 percent, and preferably no greater than about 0.05 percent is appropriate in connection with this embodiment of the invention. Decreasing the concentration of the hydroxide solution in this manner provides for satisfactory surface active agent formation while at the same time resulting in significant economies as compared to continued full-strength injection.

The hydroxide solution can be injected either by mixing the hydroxide as a component of the liquid phase of wet steam, or by mixing with wet or dry steam as by spraying the NaOH into the steam feed. Although the concentration of the hydroxide can remain constant throughout the injection, it is greatly preferred to decrease such concentration in one of the ways mentioned above.

Oil is produced through the producing well or wells, in a customary manner, and such production may occur prior to, during, and/or after, injection of the hydroxide solution in accordance with the invention.

It has been found in laboratory tests that the percentage recovery of oil, as produced in this manner, is considerably increased in many contexts of use. Further, it is found that the rate of production of such oil is accelerated. The increased efficiency and speed of production, are believed to be due to the action of the surface active agents formed in accordance with this invention, as the oil-water interface in the liquid phase.

EXAMPLE I

A laboratory model was prepared and scaled to simulate a quarter of a 2½ acre confined 5-spot pattern in a 22-foot thick reservoir, the model being packed with Ottawa sand. Thermocouples were installed to measure temperature at various points in the model.

The model was contained in a pressure vessel, and pressure was maintained in the pressure vessel at 300 p.s.i.g. Pressure in the model varied from about 200 p.s.i.g. at injection to about 70 p.s.i.g. at outlet. Xylene

was flushed in the model to remove residual fluids, and the xylene was in turn removed by acetone flush. The acetone was removed with dry air.

The model was saturated with field water, and field water and oil were injected into the model, in a proportion of 35/65, the water and oil each being taken from the Kern River Field, Kern County, Calif. The viscosity of the oil measured 823 cp at ambient temperature.

Steam of about 99 percent was prepared, and injected at a rate equivalent to between about 374–385 barrels per day for a period of time equal to 605 days.

In two runs, it was then found that 80.75 percent (first run) and 80.97 percent (second run) of the original oil in place had been recovered by the steam flooding.

EXAMPLE II

Example I was repeated except that sodium hydroxide was injected with the steam, the concentration of NaOH being 0.025 percent.

Oil recovery on the same basis was 81.56 percent after 605 days.

EXAMPLE III

Example II was repeated except that the sodium hydroxide concentration was 0.1 percent by weight and steam quality was about 97 percent.

Oil recovery was 82.5 percent of the original oil in place.

EXAMPLE IV

Example II was repeated except that the sodium hydroxide concentration was raised to 0.5 percent.

Oil recovery was increased to 84.66 percent.

EXAMPLE V

A model was prepared as in Example I. A sample of field water and oil having a viscosity of 1,776 cp was injected into the model.

Steam of greater than 99 percent was injected for a time period equivalent to 605 days at a rate equivalent to about 375 barrels per day. In a first run the oil recovered, measured as a percentage of the original oil in place, was 77.87 percent. In a second run, it was 78.79 percent.

EXAMPLE VI

Example V was repeated, injecting NaOH in an initial concentration of 0.025 percent along the steam. Oil recovery was 79.37 percent.

EXAMPLE VII

Example VI was repeated, raising the concentration of NaOH to 0.1 percent. Oil recovery was 80.71 percent.

EXAMPLE VIII

A model similar to that of Example I was prepared, except that the model was scaled to represent an 88-foot thick reservoir. Pressure conditions were similar to Example I.

The model was flushed with xylene, acetone and air in substantially the same manner as Example I.

Filtered field water and oil, each taken from the Kern River Field, were injected in an appropriate ratio

46/54, in this case the crude having a viscosity of 5,480 cp at ambient temperature.

Steam was prepared and mixed for injection into the model with boiler blow down water (pH measured at about 11.2) to achieve a steam quality of about 70 percent [referred to hereafter a "wet" steam].

The wet steam was injected at a temperature of about 316°F and at a rate equivalent to about 431–444 barrels per day, for a total period equivalent to 2,646 days. Three runs were made. At the end of the period, 57.22 percent of the original oil in place had been produced in Run No. 1, 57.22 percent also in Run No. 2, and 56.04 percent in Run No. 3.

EXAMPLE IX

Example VIII was repeated, except that 0.025 wt percent NaOH was added to the wet steam prior to injection into the model. Oil recovery was increased to 59.78 percent.

EXAMPLE X

Example IX was repeated, the NaOH concentration being raised to 0.05 percent. Oil recovery was increased remarkably to 65.58 percent.

EXAMPLE XI

Example IX was repeated, NaOH concentration being raised to 0.1 percent. Oil recovery dropped to 62.58 percent.

EXAMPLE XII

A model was prepared as in Example VIII, and the same types of crude and water as used in Example VIII were employed.

Example X was repeated except that sodium hydroxide was included in only the first 150,000 barrels of steam (on a dry steam basis) injected.

Oil recovery was 57.86 percent.

EXAMPLE XIII

Example XII was repeated, the period of sodium hydroxide injection being increased to that equivalent to 250,000 barrels of steam injected.

In two runs, oil recovery of 57.80 percent and 56.58 percent was noted.

EXAMPLE XIV

Example XII was repeated, the NaOH period being lengthened to 450,000 barrels. Oil recovery increased to 60.15 percent.

EXAMPLE XV

Example XII was repeated, the NaOH being included in the injection throughout the life of the project (about 799,000 barrels). Oil recovery increased to 61.70 percent.

EXAMPLE XVI

Example XI was repeated, except that sodium hydroxide was included in the steam injection for only the first 150,000 barrels.

Oil recovery was 59.08 percent.

EXAMPLE XVII

Example XVI was repeated, increasing the NaOH injection to 250,000 barrels.

Oil recovery was 56.41 percent.

In each of the examples XII - XVII, the total cumulative steam injection was approximately 800,000 barrels on a dry steam basis.

In all of the above examples, oil recovery was measured after at least about 10 different time intervals. The results reported above are only those obtained after the full period, but the other intermediate results tend to corroborate the final oil recovery figures as given below.

The laboratory tests performed to date, as reported in the above examples, indicated that significant improvement in oil recovery is possible by the use of sodium hydroxide injections in accordance with this invention. The results show that recovery is enhanced up to a certain point, then actually decreases as the sodium hydroxide concentration is increased above a certain level.

The tests indicate that the effect of sodium hydroxide injection is perhaps most beneficial in recovering the high viscosity crudes (e.g., Example X above) although these tests are perhaps too few to ascertain whether that would be true as a general rule.

The tests also clearly demonstrate (Examples XII through XVII) that, for a given concentration of NaOH, improvement in recovery is achieved by injecting steam including sodium hydroxide for a longer period of time (larger cumulative injection), but that the increase in recovery is small after a certain point. Judging from the results of Examples XIV and XV, it seems that this point is likely somewhere beyond one-half the life of the project.

Some additional experiments were conducted in the laboratory similar to Examples I through VII above using deionized water instead of field water; the results were not as satisfactory as when field water was used, indicating that the field water contained constituents which react with the sodium hydroxide in situ.

It was observed that the sodium hydroxide was transported through the Ottawa sand in the laboratory models as a discrete bank. From these studies and under the field conditions simulated in the laboratory, the effect of terminating the sodium hydroxide injection (Examples XII through XVII) would be noted at the producing well in about 3 to 6 months field time equivalent.

The pressure maintained in the laboratory models in the illustrative examples was not substantially greater than the pressure existing in the formations simulated by the laboratory experiments. Although the steam containing hydroxide solution could be injected at pressures somewhat higher than those existing in the formation, it is not anticipated that such pressures would be anywhere near those required to fracture the formation, which is not desired, and thus would not be substantially greater than those existing in the formation.

The above examples are exemplary, and should not be considered as limiting the invention.

Although the invention has been described in terms of preferred embodiments, it will be apparent to those skilled in the art that various changes can be made in the methods described herein, without departing from the invention as described in the appended claims.

What is claimed is:

1. A method of recovering oil from a subterranean formation having therein connate water and at least

one injection well and at least one producing well, comprising:

providing steam for injecting into said formation; mixing with said steam to form a mixture therein, small amounts of an alkali metal hydroxide, the concentration of the hydroxide in said steam being less than about 0.5 weight percent after such mixing;

injecting said steam having hydroxide therein into said reservoir at a pressure not substantially greater than formation pressure, through said injection well;

allowing said hydroxide to react in the presence of steam with said connate water in said formation, to form in situ surface active agents, said surface active agents being effective to reduce the interfacial tension between the oil and water in said formation, and to facilitate removal of the oil;

continuing the injection of said hydroxide-containing steam for a period of time sufficient to allow for the formation of a substantial amount of surface active agent; and,

producing oil through said producing well.

2. A method in accordance with claim 1, wherein said alkali metal hydroxide is sodium hydroxide, and the concentration of said sodium hydroxide is from about 0.025 percent to about 0.5 percent.

3. A method of recovering oil from a subterranean formation having therein connate water and at least one injection well and at least one producing well, comprising:

providing steam for injecting into said formation; mixing in said steam to form a mixture therein, small amounts of an alkali metal hydroxide, the concentration of the hydroxide in said steam being less than about 0.5 weight percent after such mixing;

heating said formation by injecting said steam having hydroxide therein into said reservoir at a pressure not substantially greater than formation pressure, through said injection well;

allowing said hydroxide to react in the presence of steam with said connate water in said formation, to form in situ surface active agents, said surface active agents being effective to reduce the interfacial tension between the oil and water in said formation, and to facilitate removal of the oil;

continuing the injection of said hydroxide-containing steam for a first period of time sufficient to allow for the formation of a substantial amount of surface active agent;

providing additional steam not having hydroxide material added thereto;

injecting said additional steam into said formation to drive said hydroxide-containing steam farther into said formation; and,

producing oil through said producing well.

4. A method in accordance with claim 3, wherein said alkali metal hydroxide is sodium hydroxide, and the concentration of said sodium hydroxide is from about 0.025 percent to about 0.5 percent.

5. A method in accordance with claim 3, wherein said additional steam is injected for a period of time which is in a ratio to said first period of time of less than about one.

6. A method of recovering oil from a subterranean formation having therein connate water and at least one injection well and at least one producing well, comprising:

providing steam for injecting into said formation; 5
mixing in said steam to form a mixture therein, small amounts of an alkali metal hydroxide, the concentration of the hydroxide in said steam being less than about 0.5 weight percent after such mixing; 10
injecting said steam having hydroxide therein into said reservoir through said injection well;
allowing said hydroxide to react in the presence of steam with said connate water in said formation, to form in situ surface active agents, 15
said surface active agents being effective to reduce the interfacial tension between the oil and water in said formation, and to facilitate removal of the oil;
continuing the injection of said hydroxide-containing steam, while decreasing the amount of hydroxide 20 therein, for a period of time sufficient to allow for the formation of a substantial amount of surface active agent; and,
producing oil through said producing well.

7. A method in accordance with claim 6, wherein said alkali metal hydroxide is sodium hydroxide, and the concentration of said sodium hydroxide is from about 0.025 percent to about 0.5 percent. 25

8. A method in accordance with claim 7, wherein the concentration of sodium hydroxide is between about 0.05 percent and 0.1 percent. 30

9. A method in accordance with claim 6, wherein the amount of hydroxide is continually decreased.

10. A method in accordance with claim 6, wherein said alkali metal hydroxide is sodium hydroxide, and the concentration of said hydroxide is decreased from an initial concentration of greater than about 0.1 percent to a final concentration of no greater than about 0.05 percent. 35

11. A method of recovering oil from a subterranean formation having therein connate water and at least 40

one injection well and at least one producing well, comprising:

providing steam for injecting into said formation; providing a steam mixture containing small amounts of an alkali metal hydroxide, to provide wet steam with a concentration of hydroxide of about 0.5 weight percent;

injecting said steam intermittently with and without said steam mixture into said reservoir through said injection well;

allowing said hydroxide to react in the presence of steam with said connate water in said formation, to form in situ surface active agents, said surface active agents being effective to reduce the interfacial tension between the oil and water in said formation, and to facilitate removal of the oil;

continuing the intermittent injection of said steam mixture and said steam for a period of time sufficient to allow for the formation of a substantial amount of surface active agent;

terminating the intermittent injection of said steam mixture and said steam; and producing oil through said producing well.

12. A method in accordance with claim 11, wherein said alkali metal hydroxide is sodium hydroxide, and the concentration of said sodium hydroxide is from about 0.025 percent to about 0.5 percent.

13. A method in accordance with claim 11, wherein the concentration of hydroxide in the injected steam mixture is reduced between the first hydroxide injection and the last hydroxide injection.

14. A method in accordance with claim 13, wherein said hydroxide concentration is continually reduced.

15. A method in accordance with claim 11, wherein said alkali metal hydroxide is sodium hydroxide, and the concentration of said hydroxide is reduced from first injection to final injection thereof, from at least about 0.1 percent to no greater than about 0.05 percent. 45

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,853,178 Dated December 10, 1974

Inventor(s) Chin-Wen Shen

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 25, "exchange" should read --expense--.

Column 2, line 24, "well" should read --wells--.

Column 4, line 56, "as" should read --at--.

Column 5, line 9, after "percent" insert --quality--.

Column 6, line 6, "a" should read --as--.

Column 7, line 9, "below" should read --above--.

Signed and sealed this 1st day of April 1975.

(SEAL)

Attest:

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