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STEAM INJECTION USING STEAM-LOSS INHIBITING MATERIALS

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ABSTRACT OF THE DISCLOSURE

An improved steam in situ treating process which comprises injecting into a geologic formation, either by slug injection followed by steam injection or by injection directly into a stream of steam as it is being transmitted to or being forced into a geologic formation, the following steam diverting material:

- (1) Optionally a thickening agent;
- (2) A water-sensitive colloidal swelling agent;
- (3) A stabilizing agent which impedes or delays the swelling of the swelling agent until it has impinged upon, and to some extent penetrated, the face of at least a section of the formation being treated; and
- (4) A finely divided particulated substantially water-insoluble, oil-insoluble sealing agent which supplements, or conjointly functions, with the swelling agent of (2) to plug the formation against fluid flow.

The invention pertains to the injection of live steam into geologic formations and an improved method of conducting such operations.

The use of steam in the treatment of fluid-bearing subterranean formations has grown to be of major significance in the production of such fluids as oil and gas and has potential in the production of fresh water and brines including solubilized salts or other solid minerals known as fluid mining. It has become known in some oil-producing areas as the huff-and-puff method of thermal stimulation. An interesting discussion thereof appears in the Oil and Gas Journal, vol. 64, No. 7 (Feb. 14, 1966), pp. 50 and 51.

Although the manner of using steam for such purposes is varied and is in the process of expanding into newer aspects thereof as the technology and improved techniques are developed, one of the major present uses is that of reducing the viscosity of heavy crude oil in situ so that it can, as a result thereof, be pumped or displaced, as by injected gas or water flooding, to production wells.

Despite progress in the use of steam for fluid-production from subterranean formations, there have been serious problems associated therewith which have resisted heretofore attempted approaches to their solution, salient of which is that of loss of steam to thief zones, i.e. the escape of steam from its intended course or zone into adjacent porous zones or into caverns or even, to some extent, through such zones or caverns to the atmosphere. Clearly, such loss of steam is costly and leads to a marked loss in efficiency of the operation.

The present invention provides an improvement in the treatment of geologic formations employing steam wherein loss of steam to the thief zones is effectively inhibited and the practice thereof results in increased efficiency, decreased costs, and improved production of oil or gas from the formation.

The invention is an improved steam treating process which comprises injecting into a geologic formation, either by slug injection followed by steam injection or by injection directly into a stream of steam as it is being transmitted to or being forced into a geologic formation, for thermally heating hydrocarbonaceous and mineral de-

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posits in situ, the materials hereinbelow named and described. Such materials herein may be referred to as steam-loss inhibitors or diverting agents.

The materials to be so injected, in accordance with the method of the invention, are:

- (1) Optionally a thickening agent;
- (2) A water-sensitive colloidal swelling agent;
- (3) A stabilizing agent which impedes or delays the swelling of the swelling agent until it has impinged upon, and to some extent penetrated, the face of at least a section of the formation being treated; and
- (4) A finely divided particulated substantially water-insoluble, oil-insoluble sealing agent which supplements, or conjointly functions with the swelling agent of (2) to plug the formation against fluid flow.

By the expression, water-sensitive colloidal swelling agent, is meant a material which swells upon appreciable continued contact with water (in the absence of an inhibitor or stabilizer against much swelling); a material that is commonly of an average particle size less than about 0.1 micron that tends to remain suspended for a period of time and imparts a murkiness to water when admixed therewith. Such agents tend to be thixotropic in water. Herein reference to this swelling agent, identified by numeral (2) above, will sometimes be made as the colloidal agent. Clays are the preferred colloidal agent to employ in the practice of the invention. They are well defined in Kirk-Othmer Encyclopedia, vol. V, 2nd Ed., pp. 541 to 565.

When the steam-loss inhibiting materials are injected as a slug or slugs, they are usually premixed in a carrier oil, e.g. kerosene which is miscible with the hydrocarbonaceous or mineral deposits, and then forced into the formation being treated by subsequently injected steam which may or may not carry additional steam-loss inhibitor. Alternately, the kerosene-polymer composition may be followed by a slug of liquid such as brine and thereafter by steam. In practice, according to this embodiment, the slug of steam-loss inhibitor in oil is injected periodically or intermittently between more-or-less conventional steam injection.

When the materials are injected directly into the steam, they may be premixed or injected into the steam individually as by separate injection means, preferably concurrently, although injection at closely spaced successive intervals is operable with the exception, however, that the injection of the swelling agent must not precede that of the stabilizing agent.

Although the invention is not to be construed as dependent upon a theory of the principles involved, it appears that the effective seal against undesirable passage of steam, e.g. to thief zones, is provided by the combined effect of finely divided mineral particles, e.g. silica flour, and the water-sensitive colloidal swelling agent, e.g. bentonite, within the pores or interstitial spaces of the formation.

The amount of each ingredient to employ, as well as the total amount thereof collectively, depends upon the nature or structure of the formation through which or into which steam is escaping. It is recommended that enough finely divided insoluble mineral particles be employed to provide between about 2 and about 20 pounds per square foot of porous surface of the formation exposed to the steam. The swellable agent, e.g. bentonite, may be employed in an amount of between about 1 part and 100 parts thereof per 100 parts of insoluble mineral particles. The selected ratio of colloidal material to mineral particles, for effectively sealing off the porous face of the formation varies somewhat, dependent upon conditions peculiar to the formation and steam-treating operation.

The purpose of the stabilizing agent is to inhibit the swelling of the water-sensitive colloidal agent until the

stabilizing agent has been diluted, spent, or otherwise dissipated, whereupon the colloidal agent swells. Such agents, for use in the practice of the invention, include inorganic water-soluble salts and hydrocarbon liquids. The salts are employed advantageously because they are readily lost to the formation water enabling the colloidal agent to swell. Hydrocarbon liquids, e.g. kerosene or diesel oil, are employed where the injected materials will come into contact with petroleum in the formation. Sufficient stabilizing agent, e.g. NaCl, is provided to make a brine of at least about 1.015 specific gravity with the steam when condensed. Between about 20 and 400 parts of the stabilizing agent, and usually between about 50 parts and 200 parts of the stabilizing agent, per 100 parts of the mineral particles, are employed. For practical purposes, 3 to 25 percent by weight NaCl brine, containing between 0.5 and 5.0 pounds of silica flour and between 0.1 and 2.0 pounds of clay or other colloidal material per gallon of brine, is used. Since the purpose of the gelling agent is to aid in the suspension of the mineral and clay particles, sufficient gelling agent is used to attain this objective. An amount which results in a viscosity of not less than about 10 centipoises is recommended.

As aforesuggested, the colloidal swelling agent together with the stabilizing agent to swelling and the mineral plugging agent may be injected alternately or simultaneously into the steam, either premixed or separately. On the other hand, they may be dispersed in an oil and injected as intermittent slugs or as a more-or-less continuous injection between steam injections.

Illustrative of the thickening agents to employ, when injection of the steam-loss materials is made directly into the steam, are natural gums or polymers such as guar, tragacanth, certain pretreated algae and mosses, carboxy-alkyl celluloses and related cellulosic materials; water-treated or preswelled clays; previously prepared emulsions which raise the viscosity of water or aqueous solutions; or synthetic polymers. To aid in suspending the materials in an oil when a slug type operation is practiced, such thickeners as metal soaps, e.g. aluminum oleate, naphthenates, and octoates, may be employed.

Illustrative of the water-sensitive, water-swellaable agent to employ are bentonite-type clays and certain selected polymers which may be stabilized against swelling for the time required for the steam, containing the swelling agent, to contact the portions of the formations through which steam is being lost, but which do swell upon continued contact with steam or water after the stabilizing agent has substantially lost its effectiveness.

Among such polymers are polymers of acrylamide and lightly cross-linked polymers of acrylamide and polymers of any one of urethane, sodium styrenesulfonate, vinyl toluene sulfonate, and pyrrolidone as described in application S.N. 208,252 filed July 9, 1962.

Illustrative of the stabilizing agent to employ with clays are various inorganic salts of which the alkali metal halides, e.g. NaCl, are the most abundant and economical. Other stabilizing agents for use with the swellable polymers employed are: CaCl_2 , MgCl_2 , SrCl_2 , FeCl_3 , LiCl , TiCl_4 , SnCl_4 , KF , NaI , KI , $\text{Mg}(\text{NO}_3)_2$, $\text{Fe}_2(\text{SO}_4)_3$, ZnCl_2 , $\text{Zn}(\text{NO}_3)_2$, AlCl_3 , $\text{Ca}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_2$ and mixtures and hydrates thereof.

Usually a mixture of the above salts and also usually containing lesser amounts of less common salts, is used.

Other stabilizing agents than the inorganic salts are hydrocarbon liquids, the presence of which inhibits the swelling of the colloidal agent, e.g. clay, present.

Illustrative of finely subdivided, substantially water-insoluble, oil-insoluble plugging agents to employ in the practice of the invention are pulverized silica, CaCO_3 , pumice, perlite, waste ceramic and brick material quarry dust, BaSO_4 , ground nut shells, pulverized hard resins, and the like of which at least about 90% is of a mesh size that will pass through a 325 mesh (44 micron) sieve (U.S.

Bureau of Standards Sieve Series). It is preferred that the average mesh size be not more than about 44 microns and that it have a rather wide range, say from about 1 to about 44 microns. A preponderance of the finer mesh sizes are preferred, e.g. at least about 50% of the particles of a size of not more than about 10 microns. For successful performance, a preponderance of the particles must be smaller than the pore size of the formation through which steam is being lost. To be assured of attaining this objective, it is recommended that a sample of the thief formation be obtained and both the average pore size and the pore volume be ascertained, the former usually by examination thereof under an electron microscope and the latter, usually by measurement of interstitial space by volume of fluid required to occupy a measured volume of formation.

The following procedure typifies the manner of carrying out the invention:

An oil-bearing stratum is to be treated with steam due to the presence of low API gravity crude oil which resists removal by conventional pumping or flooding. A large number of such formations exist, e.g. in California. However, when the expedient of steam injection is attempted, appreciable amounts of the injected steam are lost to one or more thief zones (porous geologic structures) adjacent to the oil-bearing stratum. To overcome this loss of steam, the invention is practiced.

The structure of the thief zone is examined. It shows that the pores in general are larger than 44 microns (i.e. particles of smaller size than those retained on a 325 mesh can be forced into such pores).

The composition for use in the treatment of a formation according to the invention is prepared as follows:

Sufficient bentonite is dispersed in fresh water to make a 1% by weight dispersion. This dispersion is allowed to hydrate for two or three hours to permit complete swelling of the bentonite. This serves as a fluid of excellent suspending properties. NaCl is then admixed with the dispersion so made in an amount of between about 3% and 20% by weight. Thereafter about 1% by weight of the dispersion, of additional bentonite and 15% to 20% by weight of silica flour, of an average particle size of less than 44 microns and preferably a major proportion less than about 10 microns, are admixed, preferably slowly, into the dispersion.

The composition so made is then either fed into a stream of steam and the resulting steam carrying the plugging agent forced into the formation, or admixed in a selected aqueous or oil base liquid and injected ahead of the steam preferably at spaced intervals.

The above example is illustrative only and is not limiting of the practice of the invention which is defined by the appended claims.

As a preferred embodiment of the invention, it is recommended that steam be started into the formation by known means, e.g. a steam generator-pump unit connected to the wellhead of a borehole which penetrates the stratum wherein the low gravity crude is located.

A composition is prepared consisting of an intimate admixture of pulverized silica (silica flour that passes through a 325 mesh sieve), water-swollen clay (as a thickening or bodying agent), NaCl (as a stabilizing agent) and anhydrous bentonite clay (as a swelling agent). The composition may be dry mixed, or, alternatively, it may be mixed in oil or in a high density NaCl brine, or the fluid may be prepared dry, including some or all of the NaCl and subsequently admixed with water or a NaCl brine. When the dry blend (silica flour, NaCl, swelling agent and thickening agent) is employed, it is blown into the steam. However, of the alternative procedures suggested, that of making a suitable NaCl brine dispersion containing a gelling or viscosity improver, admixing therewith the mineral particles and swelling agent, and injecting the brine slurry into a stream of steam, is preferred.

A sufficient amount of the ingredients are employed to penetrate preferably about four inches or more, but at least about one inch of the face of the exposed formation through which steam is escaping. For easy calculations as to the amount of swelling and sealing agents to employ, it is suggested that between about 0.1 to 1.0 pound of swelling agent, identified by (2) above, and between about 5 and 15 pounds of finely divided sealing agent, identified as (4) above, be injected per square foot of watered-out exposed surface of the formation being treated.

The rate of injection of a prepared brine slurry depends upon the volume of steam injected per hour and is adjusted accordingly after having once provided an initial seal against steam loss in the formation, as evidenced by a showing of increased steam pressure at the generator-pump unit. Provision of such seal is usually followed (as the need lessens) by a reduction in rate of steam generation, the injection of the sealing composition being reduced as less need therefor is indicated, or it may be discontinued until a need therefor is again observed. It has been found that providing a good seal in the formation substantially eliminates need for injection of additional plugging material.

The following laboratory test procedure employing a flow-cell apparatus has been found useful to ascertain the efficacy of the practice of the invention on a specific stratum.

The flow cell apparatus is constructed of two pieces of 2-inch diameter iron pipe sections about 12 inches long and having a steam lead-in line that can be controlled to allow steam to enter the upper end of either only one pipe section or both sections, the latter to provide a dual column system. Outlets are provided at the opposite end of each of the pipe sections and the sections placed in parallel, vertical relationship with each other. Both pipe sections are provided with screens near the bottom for retaining particulate material therein, e.g. sand, the sections then packed to a height of about 10 inches with formation sand which is saturated with a heavy (low API gravity) crude oil and covered with 2 inches of gravel. One of the pipe sections containing the oil-saturated sand and top gravel is then opened to steam from the line leading from a steam generator. The other section remains closed. Steam is thereby caused to enter the open section, a substantial amount condensing therein and saturating the sand and leaving a high residual amount of water therein. The permeability of the water-saturated sand when tested is found to be low, e.g. less than two darcies.

Steam is then permitted to enter concurrently into the upper ends of both pipe sections, one containing the water-saturated sands (known in oil fields as watered-out sands) and the other containing the sand saturated with the heavy crude oil. Steam flow through the dual column system will be observed to be almost entirely through the watered-out sands. The need for a method or technique to divert the steam flow from such course and into the oil sands is, therefore, clearly apparent.

The efficacy of the practice of the invention as applied to the particular oil sand being tested is then conducted as follows:

The preceding portion of the test is repeated except that after steam has been passed into one of the sections containing oil-saturated sands, a sample composition according to the invention is prepared, which is representative of one to be used in a steam treatment of a thief formation, for example, one consisting of: a NaCl brine having a specific gravity of about 1.018 and containing by weight about 1% of water-swelled clay (as a thickening agent to impart suspending properties), about 10% of silica flour of a particle size of less than 44 microns and about 1% of untreated bentonite (which together with the silica flour serves as the plugging agent). The composition so prepared is injected into the steam leading to

the dual vertical pipe sections, one containing oil sands and one containing watered-out sands. The steam carrying the composition according to the invention largely enters the watered-out sand at first, since this offers the least resistance. Within a very short time, however, the watered-out, subsequently treated sands and gravel are substantially sealed off by the composition of the invention. The injection of the composition is then discontinued and steam, which is thereafter injected, is diverted to the oil-saturated sands in the other pipe section. This test shows conclusively the efficacy of the treatment of the invention for diverting injected steam to the oil sands. The test also serves as a basis for adjusting the composition employed and calculating the amount thereof to be injected into a formation which is being treated.

The following example is illustrative of the practice of the invention.

The formation bearing crude oil of about 13° API gravity in an oil field of Kern County, Calif., was being produced by the aid of steam injection. Production from the well prior to treatment was zero barrels of oil and 164 barrels of water per day. Previous cyclic steaming had been unsuccessful. Appreciable quantities of steam were being lost through the porous and watered-out (previously steam treated) portions of the formation adjacent to those portions where oil remained in place. The oil-bearing formation was penetrated by a wellbore provided with an 8½-inch diameter cemented-in casing to a depth of 633 feet to which was secured a 6½-inch diameter slotted liner extending an additional distance to a total depth of 804 feet. The casing and liner were provided with a 2½-inch tubing extending to the level of the oil sands from which production was sought. The liner was back-packed with 6 to 9 mesh size gravel.

The pump rods and related equipment of the well were removed. The formation was flushed with 2,000 gallons of an aromatic hydrocarbon liquid and then acid-treated according to conventional practice employing 2,000 gallons of a 15% corrosion inhibited aqueous HCl solution to ascertain the extent to which acidizing affected production. No noticeable improvement resulted from either the hydrocarbon liquid flush or acid treatment.

The tubing was adjusted so its outlet was at the top of oil sands level. A steam generator unit was then located at the well site and connected to the tubing. A T and steam valve assembly was installed and connected to a supply tank, equipped with a pressurizing means and stirrer, so that the composition for diverting steam from watered-out or steamed-out parts of the formation to the residual oil-bearing portions could be provided as desired.

Steam was started into the formation and allowed to continue at an input rate of 6 million B.t.u./hour for 36 hours prior to injection of the steam-loss control material (diverting agent) according to the invention.

A diverting composition in accordance with the practice of the invention (as described below) had been prepared and placed in a supply tank. The outlet valves of the tank remained closed during the initial steam injection. The composition consisted of the following proportions by weight:

	Pounds
Bentonite -----	100
NaCl -----	100
Silica flour ranging in sizes up to 44 microns ----	400
Water (nine 42-gallon barrels at the ambient temperature of 80° F.) -----	31,375

After steam had been injected down the tubing and into the formation for about 3 days, pressure was applied to the supply tank and the valve of the T connecting the line from the diverting composition supply tank was opened and the above composition was fed into the steam

line according to the controlled intermittent schedule below:

Continuous Injection Periods	Time, o'clock	Tubing Pressure in p.s.i.g.	Total Barrels of Diverting Composition Injected	Barrels of Diverting Composition Injected Between Measurements
First.....	7:15 PM -----	225	0	Start
	8:15 PM -----	230	1.8	1.8
	9:15 PM -----	236	4.0	2.2 Stop
Second.....	12:15 AM -----	216	-----	Start
	3:15 AM -----	238	5.0	1.0 Stop
Third.....	5:50 AM -----	-----	-----	Start
	6:50 AM -----	240	7.2	2.2 Stop
Fourth.....	9:35 AM -----	-----	-----	Start
	10:35 AM -----	247	9.3	2.1
	11:25 AM -----	252	11.0	1.7 Stop
Fifth.....	12:55 PM -----	-----	-----	Start
	2:05 PM -----	265	12.7	1.7
	2:50 PM -----	280	14.5	1.8 Stop
Sixth.....	3:45 PM -----	-----	-----	Start
	5:05 PM -----	310	19.5	5.0
	9:00 PM -----	300	21.5	2.0 Stop
Seventh.....	7:10 AM -----	300	-----	Start
	7:35 AM -----	360	22.5	1.0 Stop

The table above shows that the pressure necessary to force the steam, which carried the bentonite-silica flour and NaCl diverting fluid entrained therein, gradually increased from a tube pressure of 225 p.s.i.g. to 360 p.s.i.g. Such increased pressure requirement shows that the steam treated portions of the formation, i.e. those adjacent to those portions in which oil remained, were being plugged off.

Following treatment, the well was put into production. Measurement of production showed the treatment to be very successful in that the well produced 170 barrels of oil with only 25 barrels of water per day.

Having described our invention, what we claim and desire to protect by Letters Patent is:

1. In a method of thermally heating hydrocarbonaceous and mineral materials in situ in a geologic formation, wherein steam is forced into the formation and some of the steam is lost to porous and previously steam-treated portions of the formation, the improvement comprising injecting into at least a portion of the steam, prior to its entering the formation, a steam-diverting material comprising (a) a water-sensitive swelling agent; (b) a stabilizing agent which impedes and inhibits the swelling of said swelling agent in water until after continued contact with and dilution of said stabilizing agent by steam and water; and (c) a finely divided particulate substantially water- and oil-insoluble sealing agent having an average particle size less than the average size of the pores in said formation whereby said swelling agent and sealing agent supplement one another to inhibit fluid flow into at least some of said previously steam-treated portions of the formation.

2. The method according to claim 1 wherein the proportion by weight of the water-sensitive swelling agent and the finely divided particulate substantially oil and water-insoluble sealing agent in said steam-diverting material is between about 1 part and about 100 parts of said swelling agent per 100 parts of said sealing agent, and the stabilizing agent is employed in an amount of between about 20 parts and about 400 parts by weight of said sealing agent.

3. The method according to claim 2 wherein the components of said diverting material are dry-mixed prior to injection with said steam.

4. The method according to claim 2 wherein the components of said diverting material are admixed with a liquid selected from the class consisting of oil, water, and brine and the resulting slurry is injected into the steam,

5. The method according to claim 4 wherein said diverting material is mixed with a hydrocarbon oil and the

resulting mixture is injected intermittently as slugs between steam injections.

6. The method according to claim 4 wherein said liquid is water and a thickening agent is previously admixed therewith thereby to aid in suspending said swelling and sealing agents therein.

7. The method according to claim 6 wherein said thickening agent is hydrated clay.

8. The method according to claim 2 wherein sufficient of said diverting material is injected into the steam to penetrate into the pores of the exposed faces of said porous and previously steam-treated portions of the formation to a depth at least about one inch.

9. The method according to claim 2 wherein said swelling agent is selected from water-sensitive clays and polymers.

10. The method according to claim 9 wherein said colloidal swelling agent is bentonite.

11. The method according to claim 9 wherein said swelling agent is acrylamide polymer prepared by polymerizing a monomer selected from the class consisting of at least 50% by weight acrylamide and a monomer copolymerizable therewith and between about 500 and 5,000 parts per millions by weight of a diolefinic cross-linking agent.

12. The method according to claim 2 wherein said stabilizing agent is selected from the class consisting of water-soluble inorganic salts and liquid hydrocarbons.

13. The method according to claim 12 wherein said inorganic salt consists of a major proportion of NaCl.

14. The method according to claim 2 wherein said particulate inorganic substantially insoluble sealing agent is selected from the class consisting of silica flour, BaSO₄, pumice, perlite, CaCO₃, brick, ceramic and rock particles, hard resins, and nut shell having an average particle size of less than 44 microns.

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