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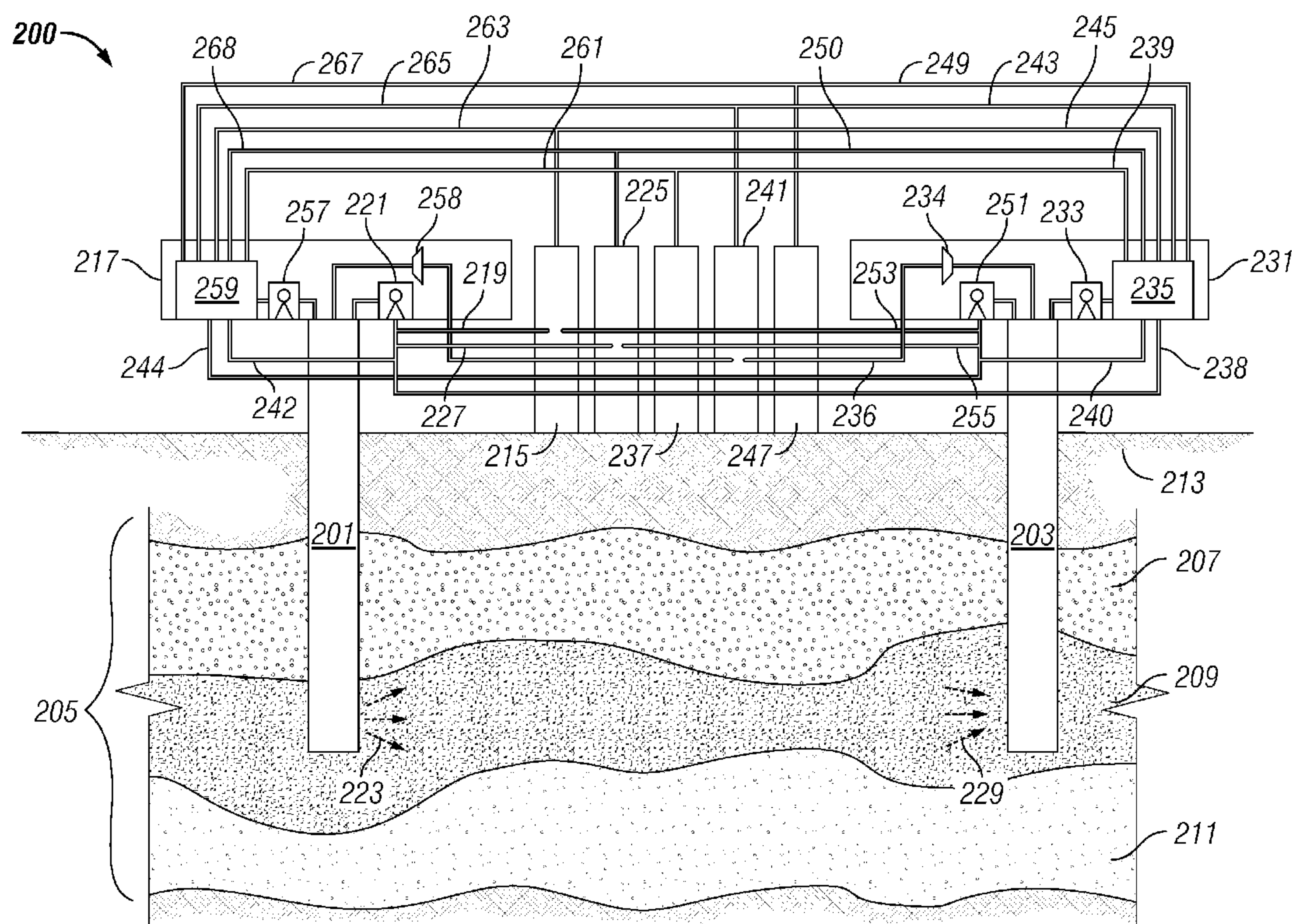
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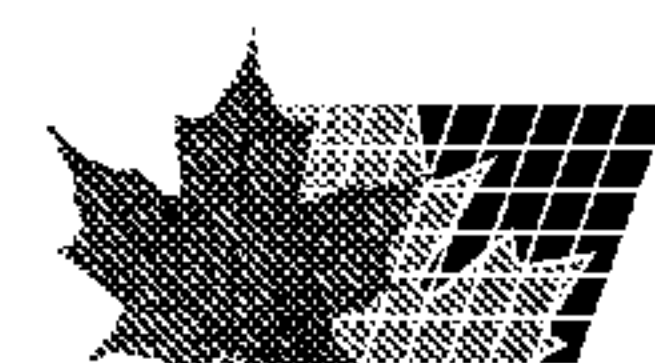
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(54) Title: PETROLEUM RECOVERY PROCESS AND SYSTEM



(57) Abrégé/Abstract:

A system and process are provided for recovering petroleum from a formation. An oil recovery formulation comprising at least 75 vol.% dimethyl sulfide is introduced into a subterranean petroleum bearing formation and petroleum is produced from the formation.



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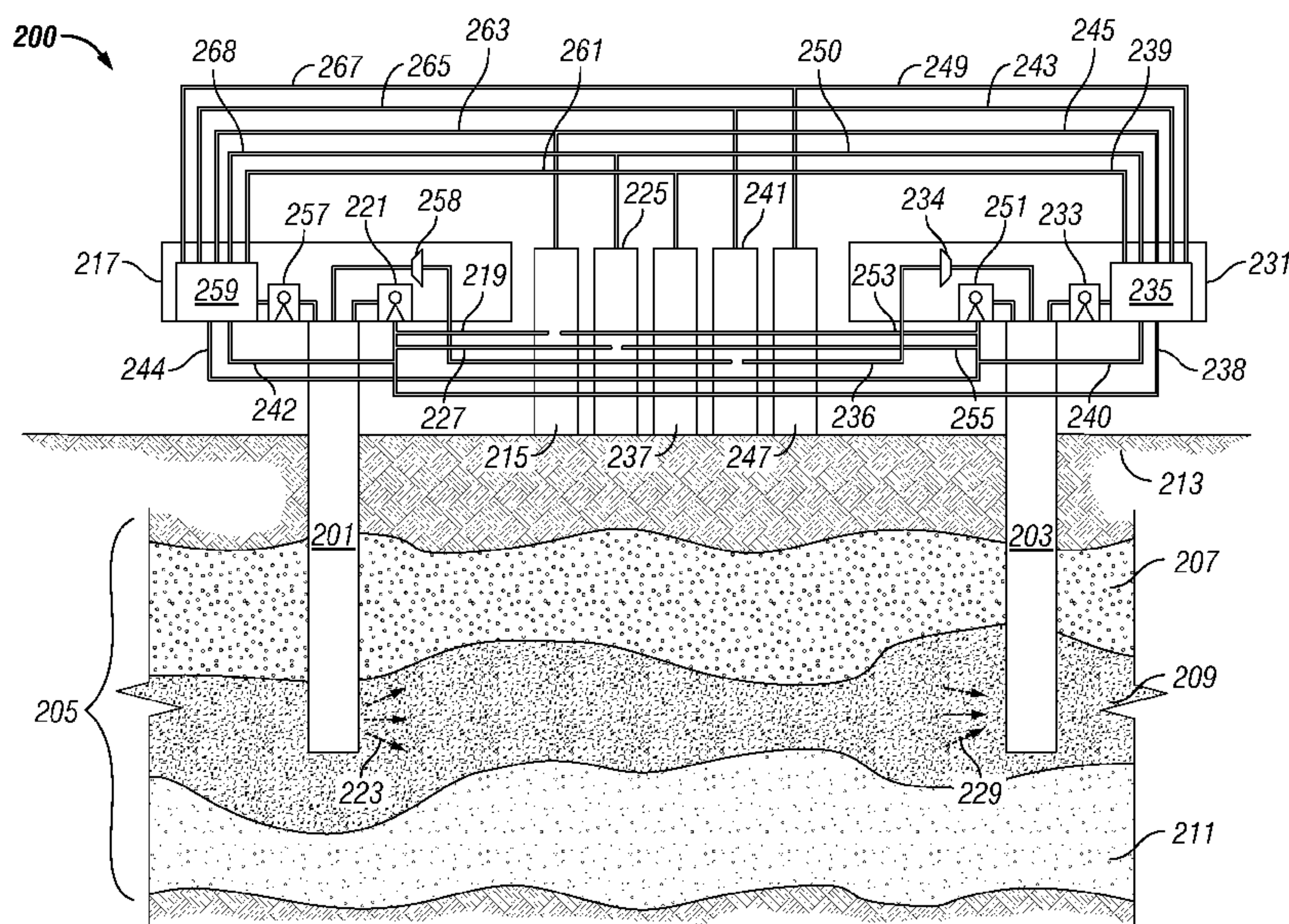
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(54) Title: PETROLEUM RECOVERY PROCESS AND SYSTEM



(57) Abstract: A system and process are provided for recovering petroleum from a formation. An oil recovery formulation comprising at least 75 vol.% dimethyl sulfide is introduced into a subterranean petroleum bearing formation and petroleum is produced from the formation.

PETROLEUM RECOVERY PROCESS AND SYSTEM

Field of the Invention

The present invention is directed to a method of recovering petroleum from a formation, in particular, the present invention is directed to a method of enhanced oil recovery from a formation.

Background of the Invention

In the recovery of petroleum from subterranean formations, it is possible to recover only a portion of the petroleum in the formation using primary recovery methods utilizing the natural formation pressure to produce the petroleum. A portion of the petroleum that cannot be produced from a formation using primary recovery methods may be produced by improved or enhanced oil recovery (EOR) methods. Improved oil recovery methods include waterflooding. EOR methods include thermal EOR, miscible displacement EOR, and chemical EOR. Thermal EOR methods heat the petroleum in a formation to reduce the viscosity of the petroleum in the formation thereby mobilizing the petroleum for recovery. Steam flooding and fire flooding are common thermal EOR methods. Miscible displacement EOR involves the injection of a compound or mixture into a petroleum-bearing formation that is miscible with petroleum in the formation to mix with the petroleum and reduce the viscosity of the petroleum, lowering its surface tension, and swelling the petroleum, thereby mobilizing the petroleum for recovery. The injected compound or mixture must be much lighter and less viscous than the petroleum in the formation—typical compounds for use as miscible EOR agents are gases such as CO₂, nitrogen, or a hydrocarbon gas such as methane. Chemical EOR involves the injection of aqueous alkaline solutions or surfactants into the formation and/or injection of polymers into the formation. The chemical EOR agent may displace petroleum from rock in the formation or free petroleum trapped in pores in the rock in the formation by reducing interfacial surface tension between petroleum and injected water to very low values thereby allowing trapped petroleum droplets to deform and flow through rock pores to form an oil bank. Polymer may be used to raise the viscosity of water to force the formed oil bank to a production well for recovery.

Relatively new EOR methods include injecting chemical solvents into a petroleum-bearing formation to mobilize the petroleum for recovery from the formation. Petroleum

in the formation is at least partially soluble in such solvents, which typically have substantially lower viscosity than the petroleum. The petroleum and chemical solvent may mix in the formation in a manner similar to a gaseous miscible EOR agent, lowering the viscosity of the petroleum, reducing the surface tension of the petroleum, and swelling the petroleum, thereby mobilizing the petroleum for production from the formation. Chemical solvents that have been utilized for this purpose include carbon disulfide and dimethyl ether.

Improvements to existing chemical solvent EOR methods are desirable. For example, chemical solvent EOR methods that increase petroleum recovery from a formation while minimizing reservoir souring, loss of EOR agent due to its solubility in formation water, and eliminate formation clean-up required as a result of the toxicity of the EOR formulation are desired.

Summary of the Invention

In one aspect, the present invention is directed to method for recovering petroleum, comprising:

providing an oil recovery formulation comprising at least 75 mol % dimethyl sulfide;

introducing the oil recovery formulation into a subterranean petroleum-bearing formation comprised of a material selected from the group consisting of a porous mineral matrix, a porous rock matrix, and a combination of a porous mineral matrix and a porous rock matrix;

contacting the oil recovery formulation with petroleum in the petroleum-bearing formation; and

producing petroleum from the formation after introduction of the oil recovery formulation into the formation.

In another aspect, the present invention is directed to a system comprising:

an oil recovery formulation comprising at least 75 mol % dimethyl sulfide;

a subterranean petroleum-bearing formation comprised of a material selected from the group consisting of a porous mineral matrix, a porous rock matrix, and a combination of a porous mineral matrix and a porous rock matrix;

a mechanism for introducing the oil recovery formulation into the subterranean petroleum-bearing formation; and

a mechanism for producing petroleum from the subterranean petroleum-bearing formation subsequent to the introduction of the oil recovery formulation into the formation.

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Brief Description of the Drawings

The drawing figures depict one or more implementations in accord with the present teachings, by way of example only, not by way of limitation. In the figures, like reference numerals refer to the same or similar elements.

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Fig. 1 is an illustration of a petroleum production system in accordance with the present invention.

Fig. 2 is an illustration of a petroleum production system in accordance with the present invention.

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Fig. 3 is an illustration of a petroleum production system in accordance with the present invention.

Fig. 4 is a diagram of a well pattern for production of petroleum in accordance with a system and process of the present invention.

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Fig. 5. is a diagram of a well pattern for production of petroleum in accordance with a system and process of the present invention.

Fig. 6 is a graph showing petroleum recovery from oil sands at 30°C using various solvents.

Fig. 7 is a graph showing petroleum recovery from oil sands at 10°C using various solvents.

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Fig. 8 is a graph showing the viscosity reducing effect of increasing concentrations of dimethyl sulfide on a West African Waxy crude oil.

Fig. 9 is a graph showing the viscosity reducing effect of increasing concentrations of dimethyl sulfide on a Middle Eastern Asphaltic crude oil.

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Fig. 10 is a graph showing the viscosity reducing effect of increasing concentrations of dimethyl sulfide on a Canadian Asphaltic crude oil.

Detailed Description of the Invention

The present invention is directed to a method and system for enhanced oil recovery from a subterranean petroleum-bearing formation utilizing an oil recovery formulation comprising at least 75 mol % dimethyl sulfide. The oil recovery formulation may be first
5 contact miscible with petroleum in the subterranean formation so that upon introduction into the formation the oil recovery formulation may completely mix with the petroleum it contacts in the formation. The oil recovery formulation may have a very low viscosity so that upon mixing with the petroleum it contacts in the subterranean formation a mixture of the petroleum and the oil recovery formulation may be produced having a significantly
10 reduced viscosity relative to the petroleum initially in place in the formation. The mixture of petroleum and oil recovery formulation may be mobilized for movement through the subterranean formation, in part due to the reduced viscosity of the mixture relative to the petroleum initially in place in the formation, where the mobilized mixture may be produced from the formation, thereby producing petroleum from the formation.

15 Certain terms used herein are defined as follows:

“Asphaltenes”, as used herein, are defined as hydrocarbons that are insoluble in *n*-heptane and soluble in toluene at standard temperature and pressure.

“Miscible”, as used herein, is defined as the capacity of two or more substances, compositions, or liquids to be mixed in any ratio without separation into two or more
20 phases.

“Fluidly operatively coupled or fluidly operatively connected”, as used herein, defines a connection between two or more elements in which the elements are directly or indirectly connected to allow direct or indirect fluid flow between the elements. The term “fluid flow”, as used herein, refers to the flow of a gas or a liquid.

25 “Petroleum”, as used herein, is defined as a naturally occurring mixture of hydrocarbons, generally in a liquid state, which may also include compounds of sulfur, nitrogen, oxygen, and metals.

“Residue”, as used herein, refers to petroleum components that have a boiling range distribution above 538 °C (1000 °F) at 0.101 MPa, as determined by ASTM Method
30 D7169

The oil recovery formulation provided for use in the method or system of the present invention is comprised of at least 75 mol % dimethyl sulfide. The oil recovery formulation may be comprised of at least 80 mol %, or at least 85 mol %, or at least 90 mol

%, or at least 95 mol %, or at least 97 mol %, or at least 99 mol % dimethyl sulfide. The oil recovery formulation may be comprised of at least 75 vol.%, or at least 80 vol.%, or at least 85 vol.%, or at least 90 vol.%, or at least 95 vol.%, or at least 97 vol.%, or at least 99 vol.% dimethyl sulfide. The oil recovery formulation may be comprised of at least 75
5 wt.%, or at least 80 wt.%, or at least 85 wt.%, or at least 90 wt.%, or at least 95 wt.%, or at least 97 wt.%, or at least 99 wt.% dimethyl sulfide. The oil recovery formulation may consist essentially of dimethyl sulfide, or may consist of dimethyl sulfide.

The oil recovery formulation provided for use in the method or system of the present invention may be comprised of one or more co-solvents that form a mixture with
10 the dimethyl sulfide in the oil recovery formulation. The one or more co-solvents are preferably miscible with dimethyl sulfide. The one or more co-solvents may be selected from the group consisting of o-xylene, toluene, carbon disulfide, dichloromethane, trichloromethane, C₃-C₈ aliphatic and aromatic hydrocarbons, natural gas condensates, hydrogen sulfide, diesel, kerosene, dimethyl ether, and mixtures thereof.

15 The oil recovery formulation provided for use in the method or system of the present invention may be first contact miscible with liquid phase petroleum compositions, preferably any liquid phase petroleum composition. In liquid phase or in gas phase the oil recovery formulation may be first contact miscible with liquid petroleum compositions including heavy crude oils, intermediate crude oils, and light crude oils, and may be first
20 contact miscible in liquid phase or in gas phase with the petroleum in the subterranean petroleum-bearing formation. The oil recovery formulation may be first contact miscible with a hydrocarbon composition, for example a liquid phase crude oil, that comprises at least 25 wt.%, or at least 30 wt.%, or at least 35 wt.%, or at least 40 wt.% hydrocarbons that have a boiling point of at least 538°C (1000°F) as determined by ASTM Method
25 D7169. The oil recovery formulation may be first contact miscible with liquid phase residue and liquid phase asphaltenes in a hydrocarbonaceous composition, for example a crude oil. The oil recovery formulation may be first contact miscible with a hydrocarbon composition that comprises less than 25 wt.%, or less than 20 wt.%, or less than 15 wt.%, or less than 10 wt.%, or less than 5 wt.% of hydrocarbons having a boiling point of at least
30 538°C (1000°F) as determined by ASTM Method D7169. The oil recovery formulation may be first contact miscible with C₃ to C₈ aliphatic and aromatic hydrocarbons containing less than 5 wt.% oxygen, less than 10 wt.% sulfur, and less than 5 wt.% nitrogen.

The oil recovery formulation may be first contact miscible with hydrocarbon compositions, for example a crude oil or liquid phase petroleum, over a wide range of viscosities. The oil recovery formulation may be first contact miscible with a hydrocarbon composition having a low or moderately low viscosity. The oil recovery formulation may be first contact miscible with a hydrocarbon composition, for example a liquid phase petroleum, having a dynamic viscosity of at most 1000 mPa s (1000 cP), or at most 500 mPa s (500 cP), or at most 100 mPa s (100 cP) at 25°C. The oil recovery formulation may also be first contact miscible with a hydrocarbon composition having a moderately high or a high viscosity. The oil recovery formulation may be first contact miscible with a hydrocarbon composition, for example a liquid phase petroleum, having a dynamic viscosity of at least 1000 mPa s (1000 cP), or at least 5000 mPa s (5000 cP), or at least 10000 mPa s (10000 cP), or at least 50000 mPa s (50000 cP), or at least 100000 mPa s (100000 cP), or at least 500000 mPa s (500000 cP) at 25°C. The oil recovery formulation may be first contact miscible with hydrocarbon composition, for example a liquid phase petroleum, having a dynamic viscosity of from 1 mPa s (1 cP) to 5000000 mPa s (5000000 cP), or from 100 mPa s (100 cP) to 1000000 mPa s (1000000 cP), or from 500 mPa s (500 cP) to 500000 mPa s (500000 cP), or from 1000 mPa s (1000 cP) to 100000 mPa s (100000 cP) at 25°C.

The oil recovery formulation provided for use in the method or system of the present invention preferably has a low viscosity. The oil recovery formulation may be a fluid having a dynamic viscosity of at most 0.35 mPa s (0.35 cP), or at most 0.3 mPa s (0.3 cP), or at most 0.285 mPa s (0.285 cP) at a temperature of 25°C.

The oil recovery formulation provided for use in the method or system of the present invention preferably has a relatively low density. The oil recovery formulation may have a density of at most 0.9 g/cm³, or at most 0.85 g/cm³.

The oil recovery formulation provided for use in the method or system of the present invention may have a relatively high cohesive energy density. The oil recovery formulation provided for use in the method or system of the present invention may have a cohesive energy density of from 300 Pa to 410 Pa, or from 320 Pa to 400 Pa.

The oil recovery formulation provided for use in the method or system of the present invention preferably is relatively non-toxic or is non-toxic. The oil recovery formulation may have an aquatic toxicity of LC₅₀ (rainbow trout) greater than 200 mg/l at 96 hours. The oil recovery formulation may have an acute oral toxicity of LD₅₀ (mouse

and rat) of from 535 mg/kg to 3700 mg/kg, an acute dermal toxicity of LD₅₀ (rabbit) of greater 5000 mg/kg, and an acute inhalation toxicity of LC₅₀ (rat) of 40250 ppm at 4 hours.

In the method of the present invention the oil recovery formulation is introduced into a subterranean petroleum-bearing formation, and the system of the present invention includes a subterranean petroleum-bearing formation. The subterranean petroleum-bearing formation comprises petroleum that may be separated and produced from the formation after contact and mixing with the oil recovery formulation. The petroleum of the subterranean petroleum-bearing formation may be first contact miscible with the oil recovery formulation. The petroleum of the subterranean petroleum-bearing formation may be a heavy oil containing at least 25 wt.%, or at least 30 wt.%, or at least 35 wt.%, or at least 40 wt.% of hydrocarbons having a boiling point of at least 538°C (1000°F) as determined in accordance with ASTM Method D7169. The heavy oil may contain at least 20 wt.% residue, or at least 25 wt.% residue, or at least 30 wt.% residue. The heavy oil may have an asphaltene content of at least at least 5 wt.%, or at least 10 wt.%, or at least 15 wt.%.

The petroleum contained in the subterranean petroleum-bearing formation may be an intermediate weight oil or a relatively light oil containing less than 25 wt.%, or less than 20 wt.%, or less than 15 wt.%, or less than 10 wt.%, or less than 5 wt.% of hydrocarbons having a boiling point of at least 538°C (1000°F). The intermediate weight oil or light oil may have an asphaltenes content of less than 5 wt.%.

The petroleum contained in the subterranean petroleum-bearing formation may have a viscosity under formation conditions (in particular, at temperatures within the temperature range of the formation) of at least 1 mPa s (1 cP), or at least 10 mPa s (10 cP), or at least 100 mPa s (100 cP), or at least 1000 mPa s (1000 cP), or at least 10000 mPa s (10000 cP). The petroleum contained in the subterranean petroleum-bearing formation may have a viscosity under formation temperature conditions of from 1 to 10000000 mPa s (1 to 10000000 cP). In an embodiment, the petroleum contained in the subterranean petroleum-bearing formation may have a viscosity under formation temperature conditions of at least 1000 mPa s (1000 cP), where the viscosity of the petroleum is at least partially, or solely, responsible for immobilizing the petroleum in the formation.

The petroleum contained in the subterranean petroleum-bearing formation may contain little or no microcrystalline wax at formation temperature conditions. Microcrystalline wax is a solid that may be only partially soluble, or may be substantially

insoluble, in the oil recovery formulation. The petroleum contained in the subterranean petroleum-bearing formation may comprise at most 3 wt.%, or at most 1 wt.%, or at most 0.5 wt.% microcrystalline wax at formation temperature conditions, and preferably microcrystalline wax is absent from the petroleum in the petroleum-bearing formation at formation temperature conditions.

The petroleum-bearing formation is a subterranean formation. The subterranean formation is comprised of one or more porous matrix materials selected from the group consisting of a porous mineral matrix, a porous rock matrix, and a combination of a porous mineral matrix and a porous rock matrix, where the porous matrix material may be located beneath an overburden at a depth ranging from 50 meters to 6000 meters, or from 100 meters to 4000 meters, or from 200 meters to 2000 meters under the earth's surface. The subterranean formation may be a subsea formation or a subsurface formation.

The porous matrix material may be a consolidated matrix material in which at least a majority, and preferably substantially all, of the rock and/or mineral that forms the matrix material is consolidated such that the rock and/or mineral forms a mass in which substantially all of the rock and/or mineral is immobile when petroleum, the oil recovery formulation, water, or other fluid is passed therethrough. Preferably at least 95 wt.% or at least 97 wt.%, or at least 99 wt.% of the rock and/or mineral is immobile when petroleum, the oil recovery formulation, water, or other fluid is passed therethrough so that any amount of rock or mineral material dislodged by the passage of the petroleum, oil recovery formulation, water, or other fluid is insufficient to render the formation impermeable to the flow of the oil recovery formulation, petroleum, water, or other fluid through the formation. The porous matrix material may be an unconsolidated matrix material in which at least a majority, or substantially all, of the rock and/or mineral that forms the matrix material is unconsolidated. The formation may have a permeability of from 0.0001 to 15 Darcies, or from 0.001 to 1 Darcy. The rock and/or mineral porous matrix material of the formation may be comprised of sandstone and/or a carbonate selected from dolomite, limestone, and mixtures thereof—where the limestone may be microcrystalline or crystalline limestone and/or chalk.

Petroleum in the subterranean petroleum-bearing formation may be located in pores within the porous matrix material of the formation. The petroleum in the subterranean petroleum-bearing formation may be immobilized in the pores within the porous matrix material of the formation, for example, by capillary forces, by interaction of

the petroleum with the pore surfaces, by the viscosity of the petroleum, or by interfacial tension between the petroleum and water in the formation.

The subterranean petroleum-bearing formation may also be comprised of water, which may be located in pores within the porous matrix material. The water in the formation may be connate water, water from a secondary or tertiary oil recovery process water-flood, or a mixture thereof. The water in the subterranean petroleum-bearing formation may be positioned to immobilize petroleum within the pores. Contact of the oil recovery formulation with the petroleum in the subterranean formation may mobilize the petroleum in the formation for production and recovery from the formation by freeing at least a portion of the petroleum from pores within the formation.

Referring now to Fig. 1, a system 100 of the present invention is shown for practicing a method of the present invention. An oil recovery formulation as described above may be provided in an oil recovery formulation storage facility 101 fluidly operatively coupled to an injection/production facility 103 via conduit 105.

Injection/production facility 103 may be fluidly operatively coupled to a well 107, which may be located extending from the injection/production facility 103 into a subterranean petroleum-bearing formation 109 such as described above comprised of one or more formation portions 111, 113, and 115 formed of porous material matrices, such as described above, located beneath an overburden 117. As shown by the down arrow in well 107, the oil recovery formulation may flow from the injection/production facility 103 through the well to be introduced into the formation 109, for example in formation portion 113, where the injection/production facility 103 and the well 107, or the well 107 itself, include(s) a mechanism for introducing the oil recovery formulation into the formation 109. The mechanism for introducing the oil recovery formulation into the formation 109 may be comprised of a pump 110 for delivering the oil recovery formulation to perforations or openings in the well through which the oil recovery formulation may be injected into the formation.

The oil recovery formulation is introduced into the subterranean formation 109, for example by being injected into the formation by pumping the oil recovery formulation into the formation. The oil recovery formulation may be introduced into the formation at a pressure above the instantaneous pressure in the formation to force the oil recovery formulation to flow into the formation. The pressure at which the oil recovery formulation is introduced into the formation may range from the instantaneous pressure in the

formation up to, but not including, the fracture pressure of the formation. The pressure at which the oil recovery formulation may be injected into the formation may range from 20% to 95%, or from 40% to 90%, of the fracture pressure of the formation. The pressure at which the oil recovery formulation is injected into the formation may range from a pressure from greater than 0 MPa to 37 MPa above the initial formation pressure as measured prior to when the injection begins.

An amount of the oil recovery formulation may be introduced into the formation to form a mobilized mixture of petroleum and the oil recovery formulation. The amount of oil recovery formulation introduced into the formation may be sufficient to form a mobilized mixture of the oil recovery formulation and petroleum that may contain at least 10 vol.%, or at least 20 vol.%, or at least 30 vol.%, or at least 40 vol.%, or at least 50 vol.%, or greater than 50 vol.% of the oil recovery formulation.

As the oil recovery formulation is introduced into the subterranean formation 109, the oil recovery formulation spreads into the formation as shown by arrows 119. Upon introduction to the formation 109, the oil recovery formulation contacts and forms a mixture with a portion of the petroleum in the formation. The oil recovery formulation is first contact miscible with the petroleum in the formation, where the oil recovery formulation mobilizes at least a portion of the petroleum in the formation upon mixing with the petroleum. The oil recovery formulation may mobilize the petroleum in the formation upon mixing with the petroleum, for example, by reducing the viscosity of the mixture relative to the native petroleum in the formation, by reducing the capillary forces retaining the petroleum in pores in the formation, by reducing the wettability of the petroleum on pore surfaces in the formation, by reducing the interfacial tension between petroleum and water in the pores in the formation, and/or by swelling the petroleum in the pores in the formation.

The respective viscosities of the oil recovery formulation and water in the subterranean formation may be on the same order of magnitude, thereby providing for a favorable displacement of the water from pores of the formation by the oil recovery formulation and corresponding ingress of the oil recovery formulation into the pores of the formation for mixing with petroleum contained in the pores. For example, the viscosity of the oil recovery formulation may range between about 0.2 cP and about 0.35 cP under formation temperature conditions. The viscosity of water of the formation may range between about 0.7 cP and about 1.1 cP under formation temperature conditions. As a

result, the oil recovery formulation is able to push the water out of the way and simultaneously contact, mix, and mobilize the petroleum.

The oil recovery formulation may be left to soak in the subterranean formation after introduction of the oil recovery formulation into the formation to mix with and mobilize the petroleum in the formation. The oil recovery formulation may be left to soak in the formation for a period of time of from 1 hour to 15 days, preferably from 5 hours to 50 hours.

Subsequent to the introduction of the oil recovery formulation into the subterranean formation 109 and after the soaking period, petroleum may be recovered and produced from the formation 109, as shown in Fig. 2. Optionally oil recovery formulation—preferably in a mixture with the petroleum—is also recovered and produced from the subterranean formation 109, and optionally gas and water from the formation are also recovered and produced from the formation 109. The system includes a mechanism for producing the petroleum, and may include a mechanism for producing the oil recovery formulation, gas, and water from the formation 109 subsequent to introduction of the oil recovery formulation into the formation, for example, after completion of introduction of the oil recovery formulation into the formation. The mechanism for recovering and producing the petroleum, and optionally the oil recovery formulation, gas, and water from the formation 109 may be comprised of a pump 112, which may be located in the injection/production facility 103 and/or within the well 107, and which draws the petroleum, and optionally the oil recovery formulation, gas, and water from the formation to deliver the petroleum, and optionally the oil recovery formulation, gas, and water, to the facility 103.

Alternatively, the mechanism for recovering and producing the petroleum and the oil recovery formulation, and optionally gas and water, from the formation 109 may be comprised of a compressor 114. The compressor 114 may be fluidly operatively coupled to a gas storage tank 129 by conduit 116, and may compress gas from the gas storage tank for injection into the formation through the well 107. The compressor 114 may compress gas from a gas storage tank for injection into the formation 109 through the well 107. The compressor may compress the gas to a pressure sufficient to drive production of petroleum and the oil recovery formulation, and optionally gas and water, from the formation via the well 107, where the appropriate pressure can be determined by conventional methods known to those skilled in the art. The compressed gas may be injected into the formation

from a different position on the well 107 than the well position at which the petroleum and optionally the oil recovery formulation, water and/or gas, are produced from the formation, for example, the compressed gas may be injected into the formation at formation portion 111 while petroleum, oil recovery formulation, water, and gas are
5 produced from the formation at formation portion 113.

Petroleum, preferably in a mixture with the oil recovery formulation, and optionally mixed with water and formation gas may be drawn from the formation portion 113 as shown by arrows 121 and produced back up the well 107 to the injection/production facility 103. The petroleum may be separated from the oil recovery formulation, water,
10 and gas in a separation unit 123. The separation unit may be comprised of a conventional liquid-gas separator for separating gas from the petroleum, oil recovery formulation, and water, a conventional hydrocarbon-water separator for separating water from petroleum and the oil recovery formulation, and a conventional distillation column for separating the oil recovery formulation from the petroleum. For ease of separation of the produced oil
15 recovery formulation from the produced petroleum, the produced oil recovery formulation may be separated from the petroleum by distillation so that the produced oil recovery formulation contains C_3 to C_8 , or C_3 to C_6 , aliphatic and aromatic hydrocarbons originating from the petroleum produced from the formation and not present in the initial oil recovery formulation. The distillation may be effected so the produced oil recovery formulation has
20 the composition of the original oil recovery formulation plus up to 25 vol.% of C_3 to C_8 aliphatic and aromatic hydrocarbons derived from the formation, where the separated produced oil recovery formulation is comprised of at least 75 mol % dimethyl sulfide.

The separated petroleum may be provided from the separation unit 123 of the injection/production facility 103 to a liquid storage tank 125, which may be fluidly
25 operatively coupled to the separation unit of the injection/production facility by conduit 127. The separated gas may be provided from the separation unit 123 of the injection/production facility 103 to the gas storage tank 129, which may be fluidly operatively coupled to the separation unit of the injection/production facility by conduit 131.

30 The separated produced oil recovery formulation, optionally containing additional C_3 to C_8 or C_3 to C_6 hydrocarbons, may be provided from the separation unit 123 of the injection/production facility to the oil recovery formulation storage facility 101, which may be fluidly operatively coupled to the separation unit of the injection/production facility by

conduit 133. Alternatively, the separated produced oil recovery formulation, optionally containing additional C₃ to C₈ or C₃ to C₆ hydrocarbons, may be provided from the separation unit 123 of the injection/production facility 103 to the injection mechanism 110 for reinjection into the formation, where the separation unit 123 may be fluidly operatively coupled to the injection mechanism 110 via conduit 118 to provide the separated produced oil recovery formulation from the separation unit 123 to the injection mechanism.

Separated water may be provided from the separation unit 123 of the injection/production facility 103 to a water tank 135, which may be fluidly operatively coupled to the separation unit of the injection/production facility by conduit 137. The water tank 135 may be fluidly operatively coupled to the injection mechanism 110 by conduit 139 for re-injection of water produced from the formation back into the subterranean formation.

After recovery and production of at least a portion of the petroleum from the subterranean formation 109, and optionally recovering and producing at least a portion of the oil recovery formulation injected into the formation, an additional portion of the oil recovery formulation may be injected into the formation to mobilize at least a portion of the petroleum remaining in the formation for recovery and production. The amount of the additional portion of oil recovery formulation injected into the formation 109 may be increased relative to the amount of oil recovery formulation injected prior to the injection of the additional portion of oil recovery formulation to increase the pore volume of the formation that is contacted by the oil recovery formulation. An additional portion of the petroleum remaining in the formation may be mobilized, recovered, and produced from the well subsequent to injection of the additional portion of the oil recovery formulation in a manner as described above. Subsequent additional portions of oil recovery formulation may be injected into the formation for further recovery and production of petroleum from the formation 109, as desired.

Referring now to Fig. 3, a system 200 of the present invention for practicing a method of the present invention is shown. The system includes a first well 201 and a second well 203 extending into a subterranean petroleum-bearing formation 205 such as described above. The subterranean petroleum-bearing formation 205 may be comprised of one or more formation portions 207, 209, and 211 formed of porous material matrices, such as described above, located beneath an overburden 213. An oil recovery formulation as described above is provided. The oil recovery formulation may be provided from an oil

recovery formulation storage facility 215 fluidly operatively coupled to a first injection/production facility 217 via conduit 219. First injection/production facility 217 may be fluidly operatively coupled to the first well 201, which may be located extending from the first injection/production facility 217 into the subterranean petroleum-bearing formation 205. The oil recovery formulation may flow from the first injection/production facility 217 through the first well to be introduced into the subterranean formation 205, for example in formation portion 209, where the first injection/production facility 217 and the first well, or the first well itself, include(s) a mechanism for introducing the oil recovery formulation into the formation. Alternatively, the oil recovery formulation may flow from the oil recovery formulation storage facility 215 directly to the first well 201 for injection into the formation 205, where the first well comprises a mechanism for introducing the oil recovery formulation into the formation. The mechanism for introducing the oil recovery formulation into the subterranean formation 205 via the first well 201—located in the first injection/production facility 217, the first well 201, or both—may be comprised of a pump 221 for delivering the oil recovery formulation to perforations or openings in the first well through which the oil recovery formulation may be introduced into the formation.

The oil recovery formulation may be introduced into the subterranean formation 205, for example by injecting the oil recovery formulation into the formation through the first well 201 by pumping the oil recovery formulation through the first well and into the formation. The pressure at which the oil recovery formulation may be injected into the subterranean formation 205 through the first well 201 may be as described above with respect to injection and production using a single well.

The volume of oil recovery formulation introduced into the subterranean formation 205 via the first well 201 may range from 0.001 to 5 pore volumes, or from 0.01 to 2 pore volumes, or from 0.1 to 1 pore volumes, or from 0.2 to 0.6 pore volumes, where the term “pore volume” refers to the volume of the formation that may be swept by the oil recovery formulation between the first well 201 and the second well 203. The pore volume may be readily be determined by methods known to a person skilled in the art, for example by modelling studies or by injecting water having a tracer contained therein through the formation 205 from the first well 201 to the second well 203.

As the oil recovery formulation is introduced into the subterranean formation 205, the oil recovery formulation spreads into the formation as shown by arrows 223. Upon introduction to the formation 205, the oil recovery formulation contacts and forms a

mixture with a portion of the petroleum in the formation. The oil recovery formulation is first contact miscible with the petroleum in the subterranean formation 205, where the oil recovery formulation may mobilize the petroleum in the formation upon contacting and mixing with the petroleum. The oil recovery formulation may mobilize the petroleum in the formation upon contacting and mixing with the petroleum, for example, by reducing the viscosity of the mixture relative to the native petroleum in the formation, by reducing the capillary forces retaining the petroleum in pores in the formation, by reducing the wettability of the petroleum on pore surfaces in the formation, by reducing the interfacial tension between petroleum and water in the pores in the formation, and/or by swelling the petroleum in the pores in the formation. As noted above, the oil recovery formulation may have a viscosity on the same order of magnitude as the viscosity of water in the formation at formation temperature conditions enabling the oil recovery formation to displace water from pores of the formation to penetrate the pores and contact, mix with, and mobilize petroleum contained therein.

The mobilized mixture of the oil recovery formulation and petroleum and any unmixed oil recovery formulation may be pushed across the subterranean formation 205 from the first well 201 to the second well 203 by further introduction of more oil recovery formulation or by introduction of an oil immiscible formulation into the formation subsequent to introduction of the oil recovery formulation into the formation. The oil immiscible formulation may be introduced into the subterranean formation 205 through the first well 201 after completion of introduction of the oil recovery formulation into the formation to force or otherwise displace the mobilized mixture of the oil recovery formulation and petroleum as well as any unmixed oil recovery formulation toward the second well 203 for production. Any unmixed oil recovery formulation may mix with and mobilize more petroleum in the formation 205 as the unmixed oil recovery formulation is displaced through the formation from the first well 201 towards the second well 203.

The oil immiscible formulation may be configured to displace the mobilized mixture of oil recovery formulation and petroleum as well as any unmixed oil recovery formulation through the formation 205. Suitable oil immiscible formulations are not first contact miscible or multiple contact miscible with petroleum in the subterranean formation 205. The oil immiscible formulation may be selected from the group consisting of an aqueous polymer fluid, water in gas or liquid form, carbon dioxide at a pressure below its

minimum miscibility pressure, nitrogen at a pressure below its minimum miscibility pressure, air, and mixtures of two or more of the preceding.

Suitable polymers for use in an aqueous polymer fluid may include, but are not limited to, polyacrylamides, partially hydrolyzed polyacrylamides, polyacrylates, ethylenic copolymers, biopolymers, carboxymethylcellulose, polyvinyl alcohols, polystyrene sulfonates, polyvinylpyrrolidones, AMPS (2-acrylamide-2-methyl propane sulfonate), combinations thereof, or the like. Examples of ethylenic copolymers include copolymers of acrylic acid and acrylamide, acrylic acid and lauryl acrylate, lauryl acrylate and acrylamide. Examples of biopolymers include xanthan gum, guar gum, alginates, and alginic acids and salts thereof. In some embodiments, polymers may be crosslinked in situ in the subterranean formation 205. In other embodiments, polymers may be generated in situ in the subterranean formation 205.

The oil immiscible formulation may be stored in, and provided for introduction into the subterranean formation 205 from, an oil immiscible formulation storage facility 225 that may be fluidly operatively coupled to the first injection/production facility 217 via conduit 227. The first injection/production facility 217 may be fluidly operatively coupled to the first well 201 to provide the oil immiscible formulation to the first well for introduction into the formation 205. Alternatively, the oil immiscible formulation storage facility 225 may be fluidly operatively coupled to the first well 201 directly to provide the oil immiscible formulation to the first well for introduction into the formation 205. The first injection/production facility 217 and the first well 201, or the first well itself, may comprise a mechanism for introducing the oil immiscible formulation into the formation 205 via the first well 201. The mechanism for introducing the oil immiscible formulation into the formation 205 via the first well 201 may be comprised of a pump or a compressor for delivering the oil immiscible formulation to perforations or openings in the first well through which the oil immiscible formulation may be injected into the formation. The mechanism for introducing the oil immiscible formulation into the formation 205 via the first well 201 may be the pump 221 utilized to inject the oil recovery formulation into the formation via the first well 201.

The oil immiscible formulation may be introduced into the subterranean formation 205, for example, by injecting the oil immiscible formulation into the formation through the first well 201 by pumping the oil immiscible formulation through the first well and into the formation. The pressure at which the oil immiscible formulation may be injected into

the subterranean formation 205 through the first well 201 may be up to, but not including, the fracture pressure of the formation, or from 20% to 99%, or from 30% to 95%, or from 40% to 90% of the fracture pressure of the formation. In an embodiment of the present invention, the oil immiscible formulation may be injected into the subterranean formation 205 at a pressure from greater than 0 MPa to 37 MPa above the formation pressure as measured prior to injection of the oil immiscible formulation.

The amount of oil immiscible formulation introduced into the subterranean formation 205 via the first well 201 following introduction of the oil recovery formulation into the formation via the first well may range from 0.001 to 5 pore volumes, or from 0.01 to 2 pore volumes, or from 0.1 to 1 pore volumes, or from 0.2 to 0.6 pore volumes, where the term “pore volume” refers to the volume of the formation that may be swept by the oil immiscible formulation between the first well and the second well. The amount of oil immiscible formulation introduced into the formation 205 should be sufficient to drive the mobilized petroleum/oil recovery formulation mixture and any unmixed oil recovery formulation across at least a portion of the formation. If the oil immiscible formulation is in liquid phase, the volume of oil immiscible formulation introduced into the subterranean formation 205 following introduction of the oil recovery formulation into the formation relative to the volume of oil recovery formulation introduced into the formation immediately preceding introduction of the oil immiscible formulation may range from 0.1:1 to 10:1 of oil immiscible formulation to oil recovery formulation, more preferably from 1:1 to 5:1 of oil immiscible formulation to oil recovery formulation. If the oil immiscible formulation is in gaseous phase, the volume of oil immiscible formulation introduced into the formation 205 following introduction of the oil recovery formulation into the formation relative to the volume of oil recovery formulation introduced into the formation immediately preceding introduction of the oil immiscible formulation may be substantially greater than a liquid phase oil immiscible formulation, for example, at least 10 or at least 20, or at least 50 volumes of gaseous phase oil immiscible formulation per volume of oil recovery formulation introduced immediately preceding introduction of the gaseous phase oil immiscible formulation.

If the oil immiscible formulation is in liquid phase, the oil immiscible formulation may have a viscosity of at least the same magnitude as the viscosity of the mobilized petroleum/oil recovery formulation mixture at formation temperature conditions to enable the oil immiscible formulation to drive the mixture of mobilized petroleum/oil recovery

formulation across the formation 205 to the second well 203. The oil immiscible formulation may have a viscosity of at least 0.8 mPa s (0.8 cP) or at least 10 mPa s (10 cP), or at least 50 mPa s (50 cP), or at least 100 mPa s (100 cP), or at least 500 mPa s (500 cP), or at least 1000 mPa s (1000 cP) at formation temperature conditions or at 25°C. If the oil immiscible formulation is in liquid phase, preferably the oil immiscible formulation has a viscosity at least one order of magnitude greater than the viscosity of the mobilized petroleum/oil recovery formulation mixture at formation temperature conditions so the oil immiscible formulation may drive the mobilized petroleum/oil recovery formulation mixture across the formation in plug flow, minimizing and inhibiting fingering of the mobilized petroleum/oil recovery formulation mixture through the driving plug of oil immiscible formulation.

The oil recovery formulation and the oil immiscible formulation may be introduced into the formation through the first well 201 in alternating slugs. For example, the oil recovery formulation may be introduced into the formation 205 through the first well 201 for a first time period, after which the oil immiscible formulation may be introduced into the formation through the first well for a second time period subsequent to the first time period, after which the oil recovery formulation may be introduced into the formation through the first well for a third time period subsequent to the second time period, after which the oil immiscible formulation may be introduced into the formation through the first well for a fourth time period subsequent to the third time period. As many alternating slugs of the oil recovery formulation and the oil immiscible formulation may be introduced into the formation through the first well as desired.

Petroleum may be mobilized for production from the subterranean formation 205 via the second well 203 by introduction of the oil recovery formulation, and optionally the oil immiscible formulation, into the formation, where the mobilized petroleum is driven through the formation for production from the second well as indicated by arrows 229 by introduction of the oil recovery formulation, and optionally the oil immiscible formulation, into the formation via the first well 201. The petroleum mobilized for production from the formation 205 may include the mobilized petroleum/oil recovery formulation mixture.

Water and/or gas may also be mobilized for production from the formation 205 via the second well 203 by introduction of the oil recovery formulation into the formation via the first well 201.

After introduction of the oil recovery formulation into the subterranean formation 205 via the first well 201, petroleum may be recovered and produced from the formation via the second well 203. The system may include a mechanism located at the second well for recovering and producing the petroleum from the subterranean formation 205

5 subsequent to introduction of the oil recovery formulation into the formation, and may include a mechanism located at the second well for recovering and producing the oil recovery formulation, the oil immiscible formulation, water, and/or gas from the formation subsequent to introduction of the oil recovery formulation into the formation. The mechanism located at the second well 203 for recovering and producing the petroleum, and
10 optionally for recovering and producing the oil recovery formulation, the oil immiscible formulation, water, and/or gas may be comprised of a pump 233, which may be located in the second injection/production facility 231 and/or within the second well 203. The pump 233 may draw the petroleum, and optionally the oil recovery formulation, the oil immiscible formulation, water, and/or gas from the formation 205 through perforations in
15 the second well 203 to deliver the petroleum, and optionally the oil recovery formulation, the oil immiscible formulation, water, and/or gas, to the second injection/production facility 231.

Alternatively, the mechanism for recovering and producing the petroleum—and optionally the oil recovery formulation, the oil immiscible formulation, gas, and water—
20 from the formation 205 may be comprised of a compressor 234 that may be located in the second injection/production facility 231. The compressor 234 may be fluidly operatively coupled to the gas storage tank 241 via conduit 236, and may compress gas from the gas storage tank for injection into the formation 205 through the second well 203. The compressor may compress the gas to a pressure sufficient to drive production of
25 petroleum—and optionally the oil recovery formulation, the oil immiscible formulation, gas, and water—from the formation via the second well 203, where the appropriate pressure may be determined by conventional methods known to those skilled in the art. The compressed gas may be injected into the formation from a different position on the second well 203 than the well position at which the petroleum—and optionally the oil
30 recovery formulation, the oil immiscible formulation, water, and gas—are produced from the formation, for example, the compressed gas may be injected into the formation at formation portion 207 while petroleum, oil recovery formulation, oil immiscible formulation, water, and gas are produced from the formation at formation portion 209.

Petroleum, optionally in a mixture with the oil recovery formulation, oil immiscible formulation, water, and/or gas may be drawn from the subterranean formation 205 as shown by arrows 229 and produced up the second well 203 to the second injection/production facility 231. The petroleum may be separated from the oil recovery formulation, gas, oil immiscible formulation (if any), and/or water in a separation unit 235 located in the second injection/production facility 231 and fluidly coupled to the mechanism 233 for recovering and producing petroleum and optionally the oil recovery formulation, the oil immiscible formulation, gas, and/or water from the formation. The separation unit 235 may be comprised of a conventional liquid-gas separator for separating gas from the petroleum, oil recovery formulation, liquid oil immiscible formulation (if any), and water; a conventional hydrocarbon-water separator for separating the petroleum and oil recovery formulation from water and optionally from liquid oil immiscible formulation; a conventional distillation column for separating the oil recovery formulation—optionally in combination with C₃ to C₈, or C₃ to C₆, aliphatic and aromatic hydrocarbons derived from the formation as discussed above—from the petroleum; and, optionally, a separator for separating liquid oil immiscible formulation from water.

The separated produced petroleum may be provided from the separation unit 235 of the second injection/production facility 231 to a liquid storage tank 237, which may be fluidly operatively coupled to the separation unit 235 of the second injection/production facility by conduit 239. The separated gas, if any, may be provided from the separation unit 235 of the second injection/production facility 231 to a gas storage tank 241, which may be fluidly operatively coupled to the separation unit 235 of the second injection/production facility 231 by conduit 243. Separated water may be provided from the separation unit 235 of the second injection/production facility 231 to a water tank 247, which may be fluidly operatively coupled to the separation unit 235 of the second injection/production facility 231 by conduit 249. Separated oil immiscible formulation, if any, may be provided from the separation unit 235 of the second injection/production facility 231 to the oil immiscible formulation storage facility 225 by conduit 250.

The separated produced oil recovery formulation, optionally containing additional C₃ to C₈ or C₃ to C₆ hydrocarbons, may be provided from the separation unit 235 of the second injection/production facility 231 to the oil recovery formulation storage unit 215, which may be fluidly operatively coupled to the separation unit 235 of the second injection/production facility 231 by conduit 245, where the produced oil recovery

formulation may be mixed with the oil recovery formulation. Alternatively, the separated oil recovery formulation may be provided from the separation unit 235 of the second injection/production facility 231 to the injection mechanism 221 via conduit 238 for re-injection into the subterranean formation 205 through the first well 201 for further mobilization and production of petroleum from the formation. Alternatively, the separated oil recovery formulation may be provided from the separation unit 235 to an injection mechanism such as pump 251 in the second injection/production facility 231 via conduit 240 for re-injection into the subterranean formation 205 through the second well 203, optionally together with fresh oil recovery formulation.

In an embodiment of a system and a method of the present invention, the first well 201 may be used for injecting the oil recovery formulation into the subterranean formation 205 and the second well 203 may be used to produce petroleum from the formation as described above for a first time period, and the second well 203 may be used for injecting the oil recovery formulation into the formation 205 to mobilize the petroleum in the formation and drive the mobilized petroleum across the formation to the first well and the first well 201 may be used to produce petroleum from the formation for a second time period, where the second time period is subsequent to the first time period. The second injection/production facility 231 may comprise a mechanism such as pump 251 that is fluidly operatively coupled the oil recovery formulation storage facility 215 by conduit 253, and optionally fluidly operatively coupled to the separation units 235 and 259 by conduits 240 and 242, respectively, to receive produced oil recovery formulation therefrom, and that is fluidly operatively coupled to the second well 203 to introduce the oil recovery formulation into the subterranean formation 205 via the second well. The pump 251 or a compressor may also be fluidly operatively coupled to the oil immiscible formulation storage facility 225 by conduit 255 to introduce the oil immiscible formulation into the formation 205 via the second well 203 subsequent to introduction of the oil recovery formulation into the formation via the second well. The first injection/production facility 217 may comprise a mechanism such as pump 257 or compressor 258 for production of petroleum, and optionally the oil recovery formulation, the oil immiscible formulation, water, and/or gas from the formation 205 via the first well 201. The first injection/production facility 217 may also include a separation unit 259 for separating petroleum, the oil recovery formulation, the oil immiscible formulation, water, and/or gas. The separation unit 259 may be comprised of a conventional liquid-gas separator for

separating gas from the petroleum, oil recovery formulation, liquid oil immiscible formulation (if any), and water; a conventional hydrocarbon-water separator for separating the petroleum and oil recovery formulation from water and optionally from liquid oil immiscible formulation; a conventional distillation column for separating the oil recovery formulation—optionally in combination with C₃ to C₈, or C₃ to C₆, aliphatic and aromatic hydrocarbons derived from the formation—from the petroleum; and, optionally, a separator for separating liquid oil immiscible formulation from water. The separation unit 259 may be fluidly operatively coupled to: the liquid storage tank 237 by conduit 261 for storage of produced petroleum in the liquid storage tank; the gas storage tank 241 by conduit 265 for storage of produced gas in the gas storage tank; and the water tank 247 by conduit 267 for storage of produced water in the water tank. Separated oil immiscible formulation, if any, may be provided from the separation unit 259 of the first injection/production facility 217 to the oil immiscible formulation storage facility 225 by conduit 268.

The separation unit 259 may be fluidly operatively coupled to the oil recovery formulation storage facility 215 by conduit 263 for storage of the produced oil recovery formulation in the oil recovery formulation storage facility 215. The separation unit 259 may be fluidly operatively coupled to either the injection mechanism 221 of the first injection/production facility 217 for injecting the oil recovery formulation into the formation 205 through the first well 201 or the injection mechanism 251 of the second injection/production facility 231 for injecting the oil recovery formulation into the formation through the second well 203 by conduits 242 and 244, respectively.

The first well 201 may be used for introducing the oil recovery formulation—and, optionally, subsequent to introduction of the oil recovery formulation via the first well, the oil immiscible formulation—into the subterranean formation 205 and the second well 203 may be used for producing petroleum from the formation for a first time period; then the second well 203 may be used for injecting the oil recovery formulation—and, optionally, subsequent to introduction of the oil recovery formulation via the second well, the oil immiscible formulation—into the formation 205 and the first well 201 may be used for producing petroleum from the formation for a second time period, where the first and second time periods comprise a cycle. Multiple cycles may be conducted which include alternating the first well 201 and the second well 203 between introducing the oil recovery formulation into the formation 205—and, optionally introducing the oil immiscible

formulation into the formation subsequent to introduction of the oil recovery formulation—
and producing petroleum from the formation, where one well is injecting and the other is
producing for the first time period, and then they are switched for a second time period. A
cycle may be from about 12 hours to about 1 year, or from about 3 days to about 6 months,
5 or from about 5 days to about 3 months. In some embodiments, the oil recovery
formulation may be introduced into the formation at the beginning of a cycle, and an oil
immiscible formulation may be introduced at the end of the cycle. In some embodiments,
the beginning of a cycle may be the first 10% to about 80% of a cycle, or the first 20% to
about 60% of a cycle, the first 25% to about 40% of a cycle, and the end may be the
10 remainder of the cycle.

Referring now to Figure 4, an array of wells 300 is illustrated. Array 300 includes
a first well group 302 (denoted by horizontal lines) and a second well group 304 (denoted
by diagonal lines). In some embodiments of the system and method of the present
invention, the first well of the system and method described above may include multiple
15 first wells depicted as the first well group 302 in the array 300, and the second well of the
system and method described above may include multiple second wells depicted as the
second well group 304 in the array 300.

Each well in the first well group 302 may be a horizontal distance 330 from an
adjacent well in the first well group 302. The horizontal distance 330 may be from about 5
20 to about 1000 meters, or from about 10 to about 500 meters, or from about 20 to about 250
meters, or from about 30 to about 200 meters, or from about 50 to about 150 meters, or
from about 90 to about 120 meters, or about 100 meters. Each well in the first well group
302 may be a vertical distance 332 from an adjacent well in the first well group 302. The
vertical distance 332 may be from about 5 to about 1000 meters, or from about 10 to about
25 500 meters, or from about 20 to about 250 meters, or from about 30 to about 200 meters, or
from about 50 to about 150 meters, or from about 90 to about 120 meters, or about 100
meters.

Each well in the second well group 304 may be a horizontal distance 336 from an
adjacent well in the second well group 304. The horizontal distance 336 may be from
30 about 5 to about 1000 meters, or from about 10 to about 500 meters, or from about 20 to
about 250 meters, or from about 30 to about 200 meters, or from about 50 to about 150
meters, or from about 90 to about 120 meters, or about 100 meters. Each well in the
second well group 304 may be a vertical distance 338 from an adjacent well in the second

well group 304. The vertical distance 338 may be from about 5 to about 1000 meters, or from about 10 to about 500 meters, or from about 20 to about 250 meters, or from about 30 to about 200 meters, or from about 50 to about 150 meters, or from about 90 to about 120 meters, or about 100 meters.

5 Each well in the first well group 302 may be a distance 334 from the adjacent wells in the second well group 304. Each well in the second well group 304 may be a distance 334 from the adjacent wells in first well group 302. The distance 334 may be from about 5 to about 1000 meters, or from about 10 to about 500 meters, or from about 20 to about 250 meters, or from about 30 to about 200 meters, or from about 50 to about 150 meters, or
10 from about 90 to about 120 meters, or about 100 meters.

Each well in the first well group 302 may be surrounded by four wells in the second well group 304. Each well in the second well group 304 may be surrounded by four wells in the first well group 302.

In some embodiments, the array of wells 300 may have from about 10 to about
15 1000 wells, for example from about 5 to about 500 wells in the first well group 302, and from about 5 to about 500 wells in the second well group 304.

In some embodiments, the array of wells 300 may be seen as a top view with first well group 302 and the second well group 304 being vertical wells spaced on a piece of land. In some embodiments, the array of wells 300 may be seen as a cross-sectional side
20 view of the subterranean formation with the first well group 302 and the second well group 304 being horizontal wells spaced within the formation.

Referring now to Figure 5, an array of wells 400 is illustrated. Array 400 includes a first well group 402 (denoted by horizontal lines) and a second well group 404 (denoted by diagonal lines). The array 400 may be an array of wells as described above with respect
25 to array 300 in Figure 4. In some embodiments of the system and method of the present invention, the first well of the system and method described above may include multiple first wells depicted as the first well group 402 in the array 400, and the second well of the system and method described above may include multiple second wells depicted as the second well group 404 in the array 400.

30 The oil recovery formulation may be injected into first well group 402, and petroleum may be recovered and produced from the second well group 404. As illustrated, the oil recovery formulation may have an injection profile 406, and petroleum may be produced from the second well group 404 having a petroleum recovery profile 408.

The oil recovery formulation may be injected into the second well group 404, and petroleum may be produced from the first well group 402. As illustrated, the oil recovery formulation may have an injection profile 408, and petroleum may be produced from the first well group 402 having a petroleum recovery profile 406.

5 The first well group 402 may be used for injecting the oil recovery formulation, and the second well group 404 may be used for producing petroleum from the formation for a first time period; then second well group 404 may be used for injecting the oil recovery formulation, and the first well group 402 may be used for producing petroleum from the formation for a second time period, where the first and second time periods comprise a
10 cycle. In some embodiments, multiple cycles may be conducted which include alternating first and second well groups 402 and 404 between injecting the oil recovery formulation, and producing petroleum and/or gas from the formation, where one well group is injecting and the other is producing for a first time period, and then they are switched for a second time period.

15 To facilitate a better understanding of the present invention, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the scope of the invention.

EXAMPLE 1

20 The quality of dimethyl sulfide as an oil recovery agent based on the miscibility of dimethyl sulfide with a crude oil relative to other compounds was evaluated. The miscibility of dimethyl sulfide, ethyl acetate, o-xylene, carbon disulfide, chloroform, dichloromethane, tetrahydrofuran, and pentane solvents with mined oil sands was measured by extracting the oil sands with the solvents at 10°C and at 30°C to determine the
25 fraction of hydrocarbons extracted from the oil sands by the solvents. The bitumen content of the mined oil sands was measured at 11 wt.% as an average of bitumen extraction yield values for solvents known to effectively extract substantially all of bitumen from oil sands—in particular chloroform, dichloromethane, o-xylene, tetrahydrofuran, and carbon disulfide. One oil sands sample per solvent per extraction temperature was prepared for
30 extraction, where the solvents used for extraction of the oil sands samples were dimethyl sulfide, ethyl acetate, o-xylene, carbon disulfide, chloroform, dichloromethane, tetrahydrofuran, and pentane. Each oil sands sample was weighed and placed in a cellulose extraction thimble that was placed on a porous polyethylene support disk in a

jacketed glass cylinder with a drip rate control valve. Each oil sands sample was then extracted with a selected solvent at a selected temperature (10°C or 30°C) in a cyclic contact and drain experiment, where the contact time ranged from 15 to 60 minutes. Fresh contacting solvent was applied and the cyclic extraction repeated until the fluid drained from the apparatus became pale brown in color.

The extracted fluids were stripped of solvent using a rotary evaporator and thereafter vacuum dried to remove residual solvent. The recovered bitumen samples all had residual solvent present in the range of from 3 wt.% to 7 wt.%. The residual solids and extraction thimble were air dried, weighed, and then vacuum dried. Essentially no weight loss was observed upon vacuum drying the residual solids, indicating that the solids did not retain either extraction solvent or easily mobilized water. Collectively, the weight of the solid or sample and thimble recovered after extraction plus the quantity of bitumen recovered after extraction divided by the weight of the initial oil sands sample plus the thimble provide the mass closure for the extractions. The calculated percent mass closure of the samples was slightly high because the recovered bitumen values were not corrected for the 3 wt.% to 7 wt.% residual solvent. The extraction experiment results are summarized in Table 1.

Table 1 Summary of Extraction Experiments of Bituminous Oil Sands with Various Fluids						
Extraction Fluid	Temperature, C	Input Solids weight, g	Output Solids weight, g	Weight Change, g	Recovered Bitumen, g	Experimental Weight Closure, %
Carbon Disulfide	30	151.1	134.74	16.4	16.43	100.0
Carbon Disulfide	10	151.4	134.62	16.8	16.62	99.9
Chloroform	30	153.7	134.3	19.4	18.62	99.5
Chloroform	10	156.2	137.5	18.7	17.85	99.5
Dichloromethane	30	155.8	138.18	17.7	16.30	99.1
Dichloromethane	10	155.2	136.33	18.9	17.66	99.2
o-Xylene	30	156.1	136.58	19.5	17.37	98.6
o-Xylene	10	154.0	136.66	17.3	17.36	100.0
Tetrahydrofuran	30	154.7	136.73	18.0	17.67	99.8
Tetrahydrofuran	10	154.7	136.98	17.7	16.72	99.4
Ethyl Acetate	30	153.5	135.81	17.7	11.46	96.0
Ethyl Acetate	10	155.7	144.51	11.2	10.32	99.4
Pentane	30	154.0	139.11	14.9	13.49	99.1
Pentane	10	152.7	138.65	14.1	13.03	99.3
Dimethyl Sulfide	30	154.2	137.52	16.7	16.29	99.7
Dimethyl Sulfide	10	151.7	134.77	16.9	16.55	99.7

Fig. 6 provides a graph plotting the weight percent yield of extracted bitumen as a function of the extraction fluid at 30°C applied with a correction factor for residual extraction fluid in the recovered bitumen, and Fig. 7 provides a similar graph for extraction at 10°C without a correction factor. Figs. 6 and 7 and Table 1 show that dimethyl sulfide is comparable for recovering bitumen from an oil sand material with the best known fluids for recovering bitumen from an oil sand material—o-xylene, chloroform, carbon disulfide, dichloromethane, and tetrahydrofuran—and is significantly better than pentane and ethyl acetate.

The bitumen samples extracted at 30°C from each oil sands sample were evaluated by SARA analysis to determine the saturates, aromatics, resins, and asphaltenes composition of the bitumen samples extracted by each solvent. The results are shown in Table 2.

Table 2				
SARA Analysis of Extracted Bitumen Samples as a Function of Extraction Fluid				
	Oil Composition Normalized Weight Percent			
Extraction Fluid	Saturates	Aromatics	Resins	Asphaltenes
Ethyl Acetate	21.30	53.72	22.92	2.05
Pentane	22.74	54.16	22.74	0.36
Dichloromethane	15.79	44.77	24.98	14.45
Dimethyl Sulfide	15.49	47.07	24.25	13.19
Carbon Disulfide	18.77	41.89	25.49	13.85
o-Xylene	17.37	46.39	22.28	13.96
Tetrahydrofuran	16.11	45.24	24.38	14.27
Chloroform	15.64	43.56	25.94	14.86

The SARA analysis showed that pentane and ethyl acetate were much less effective for extraction of asphaltenes from oil sands than are the known highly effective bitumen extraction fluids dichloromethane, carbon disulfide, o-xylene, tetrahydrofuran, and chloroform. The SARA analysis also showed that dimethyl sulfide has excellent miscibility properties for even the most difficult hydrocarbons—asphaltenes.

The data showed that dimethyl sulfide is generally as good as the recognized very good bitumen extraction fluids for recovery of bitumen from oil sands, and is highly compatible with saturates, aromatics, resins, and asphaltenes.

EXAMPLE 2

The quality of dimethyl sulfide as an oil recovery agent based on the crude oil viscosity lowering properties of dimethyl sulfide was evaluated. Three crude oils having widely disparate viscosity characteristics—an African Waxy crude, a Middle Eastern asphaltic crude, and a Canadian asphaltic crude—were blended with dimethyl sulfide. Some properties of the three crudes are provided in Table 3.

Table 3			
Crude Oil Properties			
	African Waxy crude	Middle Eastern Asphaltic crude	Canadian Asphaltic Crude
Hydrogen (wt.%)	13.21	11.62	10.1
Carbon (wt.%)	86.46	86.55	82
Oxygen (wt.%)	na	na	0.62
Nitrogen (wt.%)	0.166	0.184	0.37
Sulfur (wt.%)	0.124	1.61	6.69
Nickel (ppm wt.)	32	14.2	70
Vanadium (ppm wt.)	1	11.2	205
microcarbon residue (wt.%)	na	8.50	12.5
C ₅ Asphaltenes (wt.%)	<0.1	na	16.2
C ₇ Asphaltenes (wt.%)	<0.1	na	10.9
Density (g/ml) (15.6°C)	0.88	0.9509	1.01
API Gravity (15.6°C)	28.1	17.3	8.5
Water (Karl Fisher Titration) (wt.%)	1.65	<0.1	<0.1
TAN-E (ASTM D664) (mg KOH/g)	1.34	4.5	3.91
Volatiles Removed by Topping, wt%	21.6	0	0
Saturates in Topped Fluid, wt.%	60.4	41.7	12.7

Aromatics in Topped Fluid, wt.%	31.0	40.5	57.1
Resin in Topped Fluid, wt.%	8.5	14.5	17.1
Asphaltenes in Topped Fluid, wt.%	0.1	3.4	13.1
Boiling Range Distribution			
Initial Boiling Point - 204°C (wt.%)	8.5	3.0	0
204°C (400°F) - 260°C (wt.%)	9.5	5.8	1.0
260°C (500°F) - 343°C (wt.%)	16.0	14.0	14.0
343°C (650°F) - 538°C (wt.%)	39.5	42.9	38.0
>538°C (wt.%)	26.5	34.3	47.0

A control sample of each crude was prepared containing no dimethyl sulfide, and samples of each crude were prepared and blended with dimethyl sulfide to prepare crude samples containing increasing concentrations of dimethyl sulfide. Each sample of each of the crudes was heated to 60°C to dissolve any waxes therein and to permit weighing of a homogeneous liquid, weighed, allowed to cool overnight, then blended with a selected quantity of dimethyl sulfide. The samples of the crude/dimethyl sulfide blend were then heated to 60°C and mixed to ensure homogeneous blending of the dimethyl sulfide in the samples. Absolute (dynamic) viscosity measurements of each of the samples were taken using a rheometer and closed cup sensor assembly. Viscosity measurements of each of the samples of the West African waxy crude and the Middle Eastern asphaltic crude were taken at 20°C, 40°C, 60°C, 80°C, and then again at 20°C after cooling from 80°C, where the second measurement at 20°C is taken to measure the viscosity without the presence of waxes since wax formation occurs slowly enough to permit viscosity measurement at 20°C without the presence of wax. Viscosity measurements of each of the samples of the Canadian asphaltic crude were taken at 5°C, 10°C, 20°C, 40°C, 60°C, 80°C, The measured viscosities for each of the crudes are shown in Tables 4, 5, and 6 below.

Table 4 Viscosity (mPa s) of West African Waxy Crude vs. Temperature at Various levels of Dimethyl Sulfide Diluent					
DMS, wt.%	20°C	40°C	60°C	80°C	20°C
0.00	128.8	34.94	15.84	9.59	114.4
1.21	125.8	30.94	14.66	8.92	100.1
2.48	122.3	30.53	13.66	8.44	89.23
5.03	78.37	20.24	10.45	6.55	55.21
7.60	60.92	17.08	9.29	6.09	40.89
9.95	44.70	13.03	7.58	5.04	30.61
15.13	23.96	8.32	4.97	3.38	17.64
19.30	15.26	6.25	4.05	2.92	12.06

Table 5 Viscosity (mPa s) of Middle Eastern Asphaltic Crude vs. Temperature at Various levels of Dimethyl Sulfide Diluent					
DMS, wt.%	20°C	40°C	60°C	80°C	20°C
0.00	2936.3	502.6	143.6	56.6	2922.7
1.3	1733.8	334.5	106.7	44.6	1624.8
2.6	1026.6	219.9	76.5	34.3	881.1
5.3	496.5	134.2	52.2	25.5	503.5
7.6	288.0	89.4	37.4	19.3	290.0
10.1	150.0	52.4	24.5	13.5	150.5
15.2	59.4	25.2	13.6	8.2	60.7
20.1	29.9	14.8	8.7	5.7	31.0

Table 6 Viscosity (mPa s) of Topped Canadian Asphaltic Crude vs. Temperature at Various levels of Dimethyl Sulfide Diluent						
DMS, wt.%	5 °C	10°C	20°C	40°C	60°C	80°C
0.00			579804	28340	3403	732
1.43			212525	14721	2209	538
2.07			134880	10523	1747	427
4.87			28720	3235	985	328
8.01			5799	982	275	106

9.80			2760	571	173	73
14.81	1794	1155	548	159	64	32
19.78			188	69	33	19
29.88	113	81	51	22	13	8
39.61	23	20	14	8	6	4

Figs. 8, 9, and 10 show plots of Log[Log(Viscosity)] v. Log[Temperature °K] derived from the measured viscosities in Tables 4, 5, and 6, respectively, illustrating the effect of increasing concentrations of dimethyl sulfide in lowering the viscosity of the crude samples.

The measured viscosities and the plots show that dimethyl sulfide is effective for significantly lowering the viscosity of a crude oil over a wide range of initial crude oil viscosities.

EXAMPLE 3

Incremental recovery of oil from a formation core using an oil recovery formulation consisting of dimethyl sulfide following oil recovery from the core by water-flooding was measured to evaluate the effectiveness of DMS as a tertiary oil recovery agent.

Two 5.02 cm long Berea sandstone cores with a core diameter of 3.78 cm and a permeability between 925 and 1325 mD were saturated with a brine having a composition as set forth in Table 7.

TABLE 7

Brine Composition

Chemical component	CaCl ₂	MgCl ₂	KCl	NaCl	Na ₂ SO ₄	NaHCO ₃
Concentration (kppm)	0.386	0.523	1.478	28.311	0.072	0.181

After saturation of the cores with brine, the brine was displaced by a Middle Eastern Asphaltic crude oil having the characteristics as set forth above in Table 3 to saturate the cores with oil.

Oil was recovered from each oil saturated core by the addition of brine to the core under pressure and by subsequent addition of DMS to the core under pressure. Each core was treated as follows to determine the amount of oil recovered from the core by addition of brine followed by addition of DMS. Oil was initially displaced from the core by

addition of brine to the core under pressure. A confining pressure of 1 MPa was applied to the core during addition of the brine, and the flow rate of brine to the core was set at 0.05 ml/min. The core was maintained at a temperature of 50°C during displacement of oil from the core with brine. Oil was produced and collected from the core during the displacement of oil from the core with brine until no further oil production was observed (24 hours).

After no further oil was displaced from the core by the brine, oil was displaced from the core by addition of DMS to the core under pressure. DMS was added to the core at a flow rate of 0.05 ml/min for a period of 32 hours for the first core and for a period of 15 hours for the second core. Oil displaced from the core during the addition of DMS to the core was collected separately from the oil displaced by the addition of brine to the core.

The oil samples collected from each core by brine displacement and by DMS displacement were isolated from water by extraction with dichloromethane, and the separated organic layer was dried over sodium sulfate. After evaporation of volatiles from the separated, dried organic layer of each oil sample, the amount of oil displaced by brine addition to a core and the amount of oil displaced by DMS addition to the core were weighed. Volatiles were also evaporated from a sample of the Middle Eastern asphaltic oil to be able to correct for loss of light-end compounds during evaporation. Table 8 shows the amount of oil produced from each core by brine displacement followed by DMS displacement.

TABLE 8

	Oil produced Brine displacement (ml)	Oil produced Brine displacement (of % oil initially in core)	Oil produced DMS displacement (ml)	Oil produced DMS displacement (of % oil initially in core)
Core 1	4.9	45	3.5	32
Core 2	5.0	45	3.3	30

As shown in Table 8, DMS is quite effective for recovering an incremental quantity of oil from a formation core after recovery of oil from the core by waterflooding with a brine solution—recovering approximately 60% of the oil remaining in the core after the waterflood.

The present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are

illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. While systems and methods are

5 described in terms of “comprising,” “containing,” or “including” various components or steps, the compositions and methods can also “consist essentially of” or “consist of” the various components and steps. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, “from a to b,” or,

10 equivalently, “from a-b”) disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Whenever a numerical range having a specific lower limit only, a specific upper limit only, or a specific upper limit and a specific lower limit is disclosed, the range also includes any numerical value “about” the specified lower limit and/or the specified upper limit. Also, the terms in the claims have

15 their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles “a” or “an”, as used in the claims, are defined herein to mean one or more than one of the element that it introduces.

CLAIMS

1. A method for producing petroleum, comprising:
providing an oil recovery formulation comprising at least 75 mol % dimethyl sulfide;
5 introducing the oil recovery formulation into a subterranean petroleum-bearing formation
comprised of a material selected from the group consisting of a porous mineral matrix, a
porous rock matrix, and a combination of a porous mineral matrix and a porous rock
matrix;
contacting the oil recovery formulation with petroleum in the petroleum-bearing formation;
10 and
producing petroleum from the formation after introduction of the oil recovery formulation
into the formation and after contacting the oil recovery formulation with petroleum in the
formation.
- 15 2. The method of claim 1 wherein the oil recovery formulation is first contact miscible
with liquid phase petroleum in, or from, the formation.
3. The method of claim 1 wherein the oil recovery formulation is first contact miscible
with liquid phase petroleum.
20
4. The method of claim 3 wherein the oil recovery formulation in liquid phase is first
contact miscible with a liquid phase petroleum composition that comprises at least 25
wt.%, or at least 30 wt.%, or at least 35 wt.% hydrocarbons having a boiling point of at
least 538°C as measured by ASTM Method D7169.
25
5. The method of claim 3 wherein the oil recovery formulation in liquid phase is first
contact miscible with a liquid phase petroleum composition that comprises less than 25
wt.%, or less than 20 wt. %, or less than 15 wt.%, or less than 10 wt.%, or less than 5 wt.%
hydrocarbons having a boiling point of at least 538°C as measured by ASTM Method
30 D7169.
6. The method of claim 1 or any of claims 2-5 wherein the oil recovery formulation
has a cohesive energy density of from 300 Pa to 410 Pa .

7. The method of claim 1 or any of claims 2-6 wherein from 0.001 to 0.6 pore volumes of the oil recovery formulation is introduced into the subterranean petroleum-bearing formation.

5 8. The method of claim 1 or any of claims 2-7 wherein the porous mineral or rock matrix is a consolidated matrix comprising sandstone, limestone, or dolomite.

9. The method of claim 1 or any of claims 2-8 wherein the oil recovery formulation has a dynamic viscosity of at most 0.35 mPa s (0.3 cP) , or at most 0.3 mPa s at 25°C.

10

10. The method of claim 1 or any of claims 2-9 wherein the oil recovery formulation has a density of at most 0.9 g/cm³.

11. The method of claim 1 or any of claims 2-10 wherein the oil recovery formulation
15 is introduced into the formation by injection via a first well extending into the formation.

12. The method of claim 11 wherein the petroleum is produced from the formation via the first well.

20 13. The method of claim 11 wherein the petroleum is produced from the formation via a second well extending into the formation.

14. The method of claim 1 or any of claims 2-12 wherein the oil recovery formulation is produced from the formation.

25

15. The method of claim 1 wherein the oil recovery formulation has an aquatic toxicity of LC₅₀ >200 mg/l at 96 hours.

16. The method of claim 1 or any of claims 2-15 further comprising the step of
30 introducing an oil immiscible formulation into the subterranean petroleum-bearing formation subsequent to the introduction of the oil recovery formulation into the formation.

17. A system, comprising:

an oil recovery formulation comprising at least 75 mol % dimethyl sulfide;

a subterranean petroleum-bearing formation comprised of a material selected from the group consisting of a porous mineral matrix, a porous rock matrix, and a combination
5 of a porous mineral matrix and a porous rock matrix;

a mechanism for introducing the oil recovery formulation into the subterranean petroleum-bearing formation; and

a mechanism for producing petroleum from the subterranean petroleum-bearing formation subsequent to the introduction of the oil recovery formulation into the formation.

10

18. The system of claim 17, wherein the mechanism for introducing the oil recovery formulation into the subterranean petroleum-bearing formation is located at a first well extending into the subterranean formation.

15

19. The system of claim 18 wherein the mechanism for producing petroleum from the subterranean petroleum-bearing formation is located at the first well extending into the subterranean formation.

20

20. The system of claim 18 wherein the mechanism for producing petroleum from the subterranean petroleum-bearing formation is located at a second well extending into the subterranean formation.

25

21. The system of claim 17 or any of claims 18-20 wherein the oil recovery formulation is first contact miscible with liquid phase petroleum.

22. The system of claim 17 or any of claims 18-21 wherein the oil recovery formulation is first contact miscible with petroleum in, or from, the formation.

30

23. The system of claim 17 or any of claims 18-22 wherein the oil recovery formulation is first contact miscible with a liquid phase crude oil that comprises at least 25 wt.%, or at least 30 wt.%, or at least 35 wt.% hydrocarbons having a boiling point of at least 538°C as measured by ASTM Method D7169.

24. The system of claim 17 or any of claims 18-22 wherein the oil recovery formulation is first contact miscible with a liquid phase crude oil that comprises less than 25 wt.%, or less than 20 wt. %, or less than 15 wt.%, or less than 10 wt.%, or less than 5 wt.% hydrocarbons having a boiling point of at least 538°C as measured by ASTM Method D7169.
25. The system of claim 17 or any of claims 18-24 further comprising:
an oil immiscible formulation; and
a mechanism for introducing the oil immiscible formulation into the subterranean petroleum-bearing formation.

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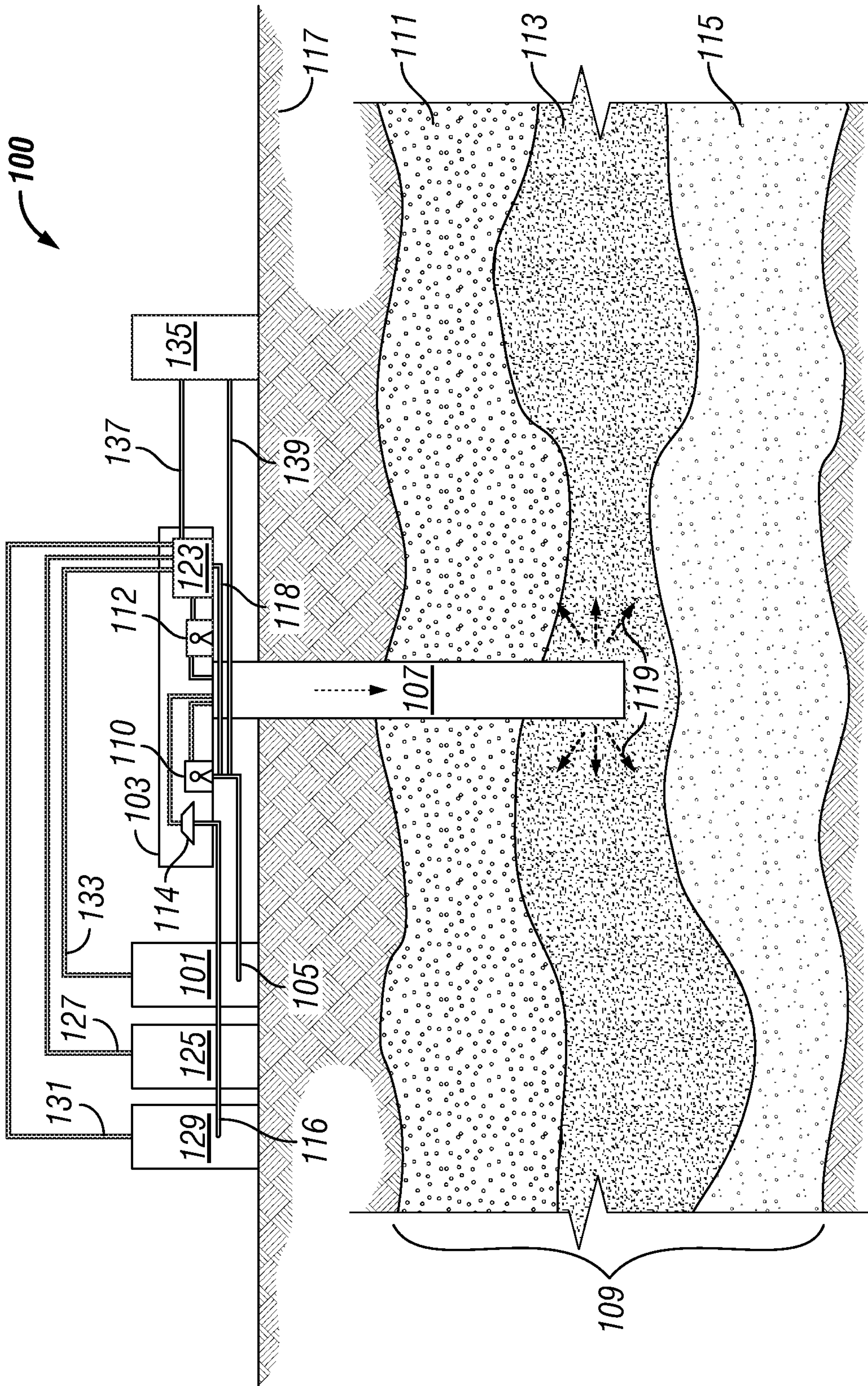


FIG. 1

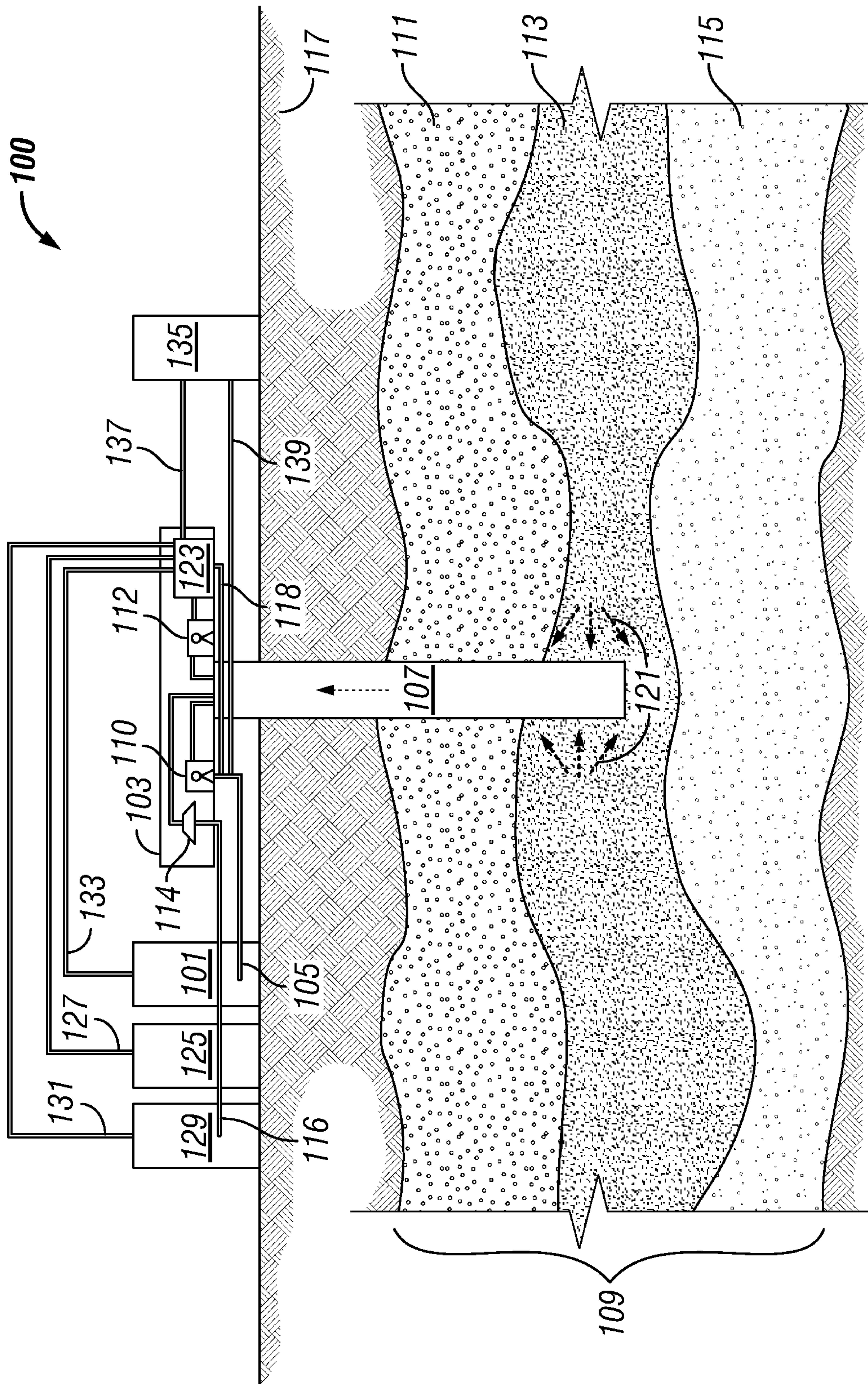


FIG. 2

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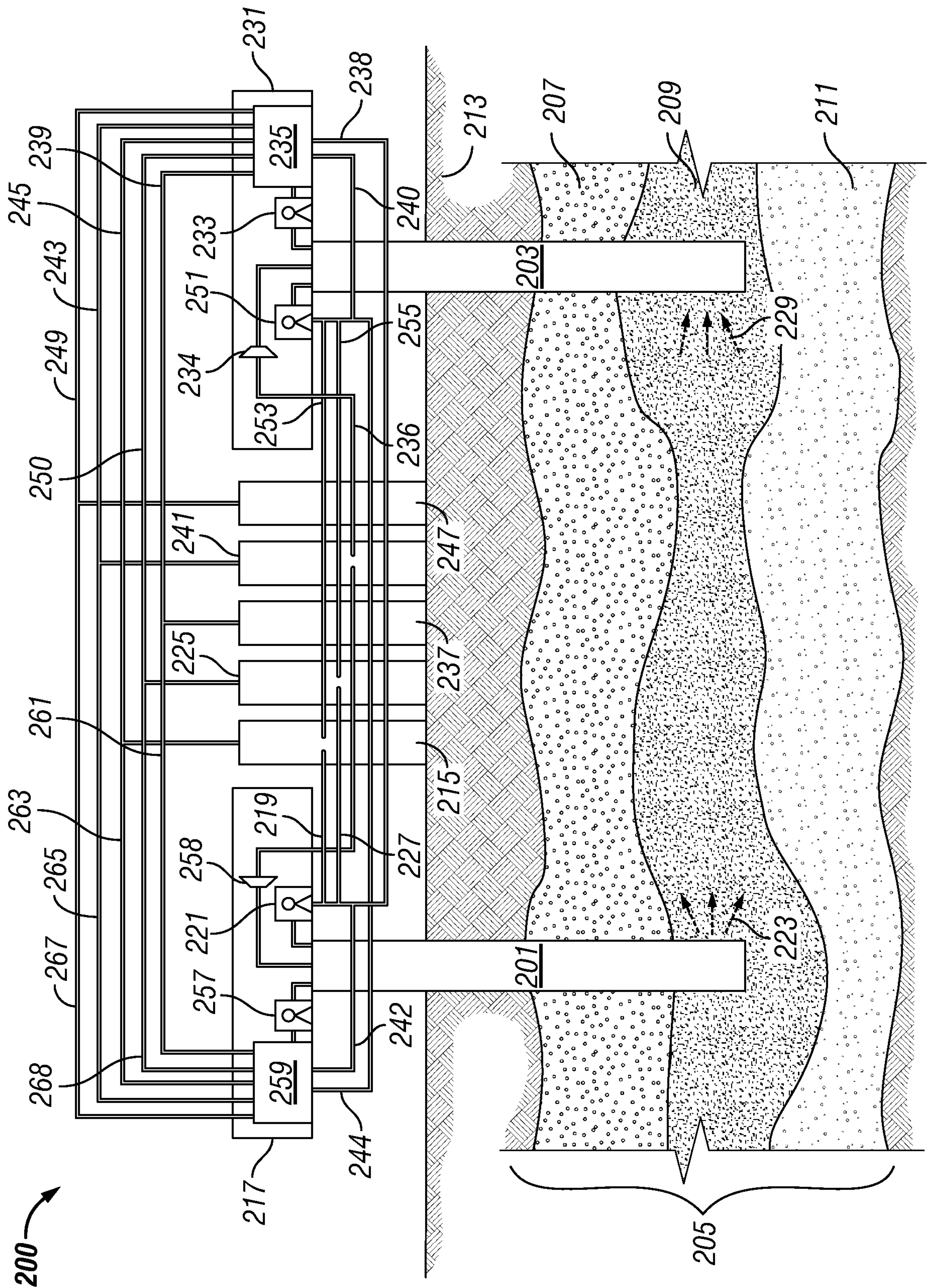
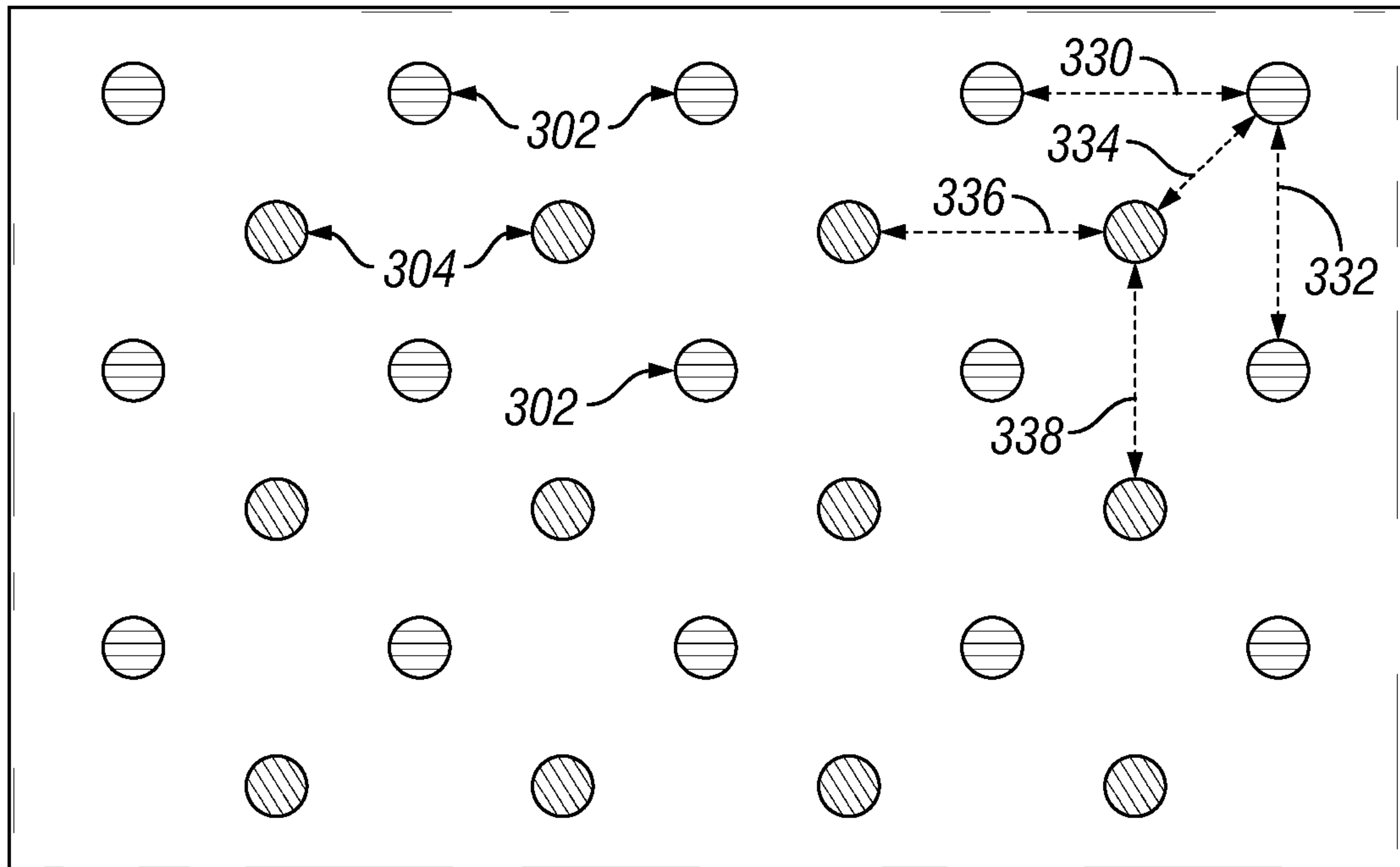
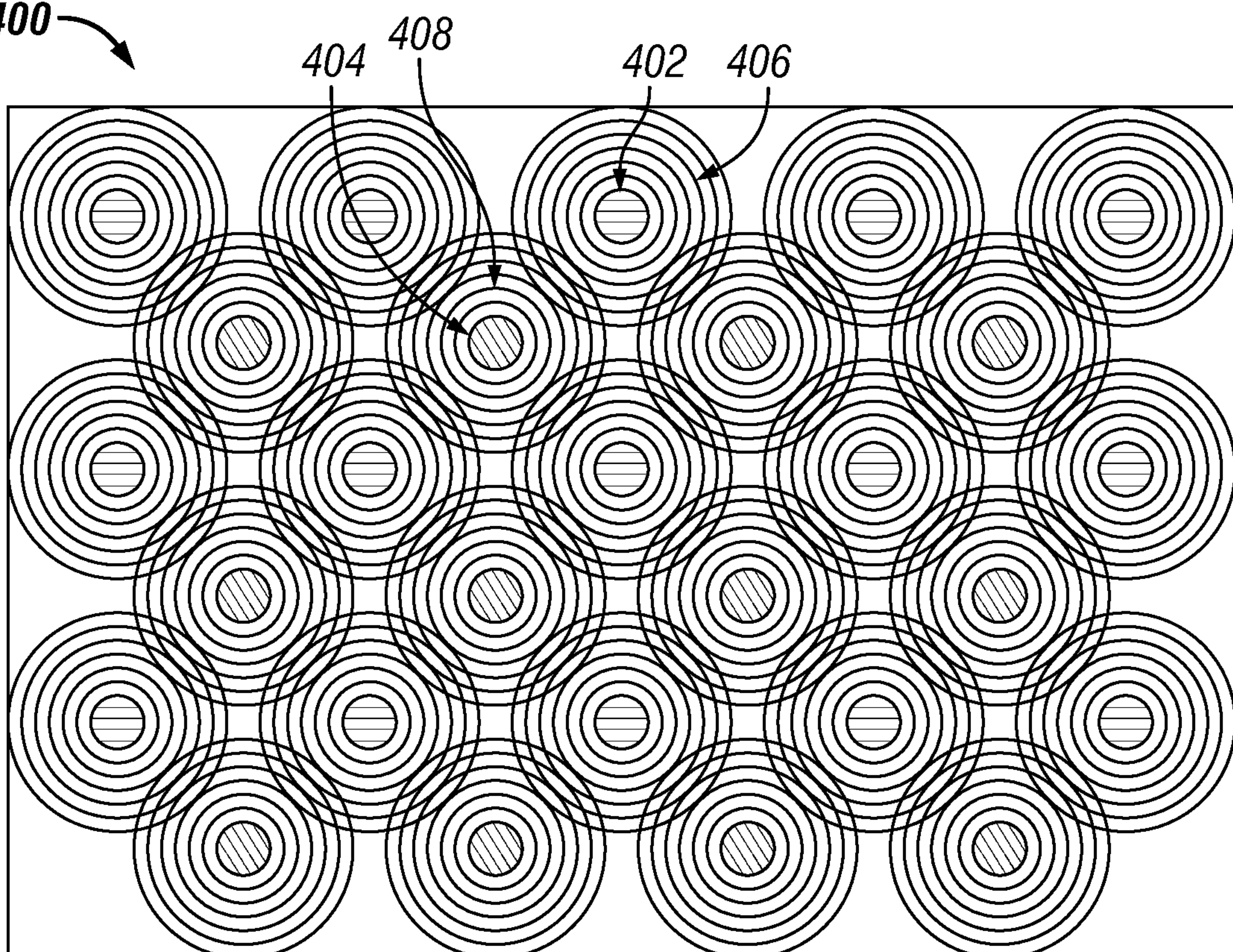


FIG. 3

4/9**300** →**FIG. 4****400** →**FIG. 5**

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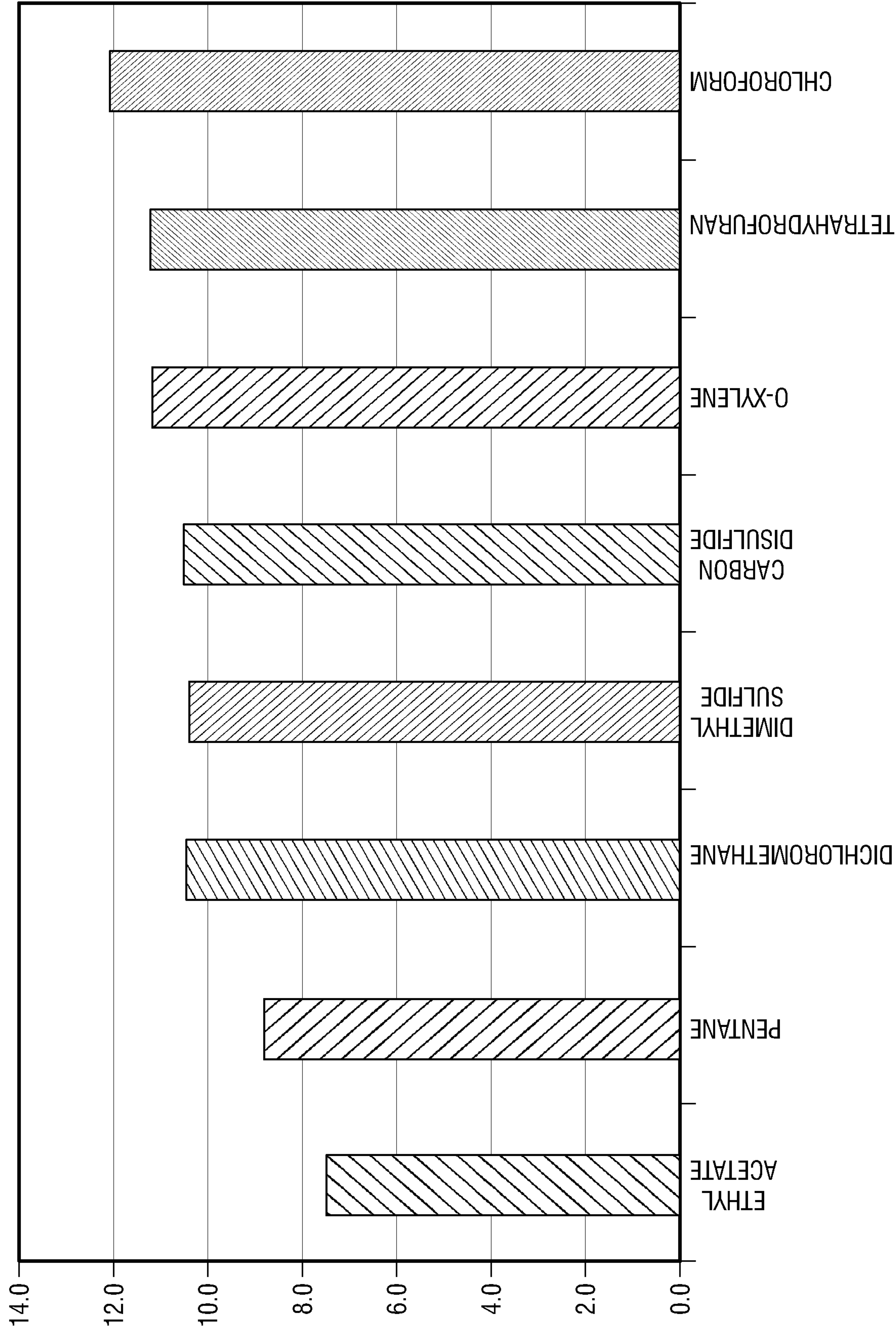


FIG. 6

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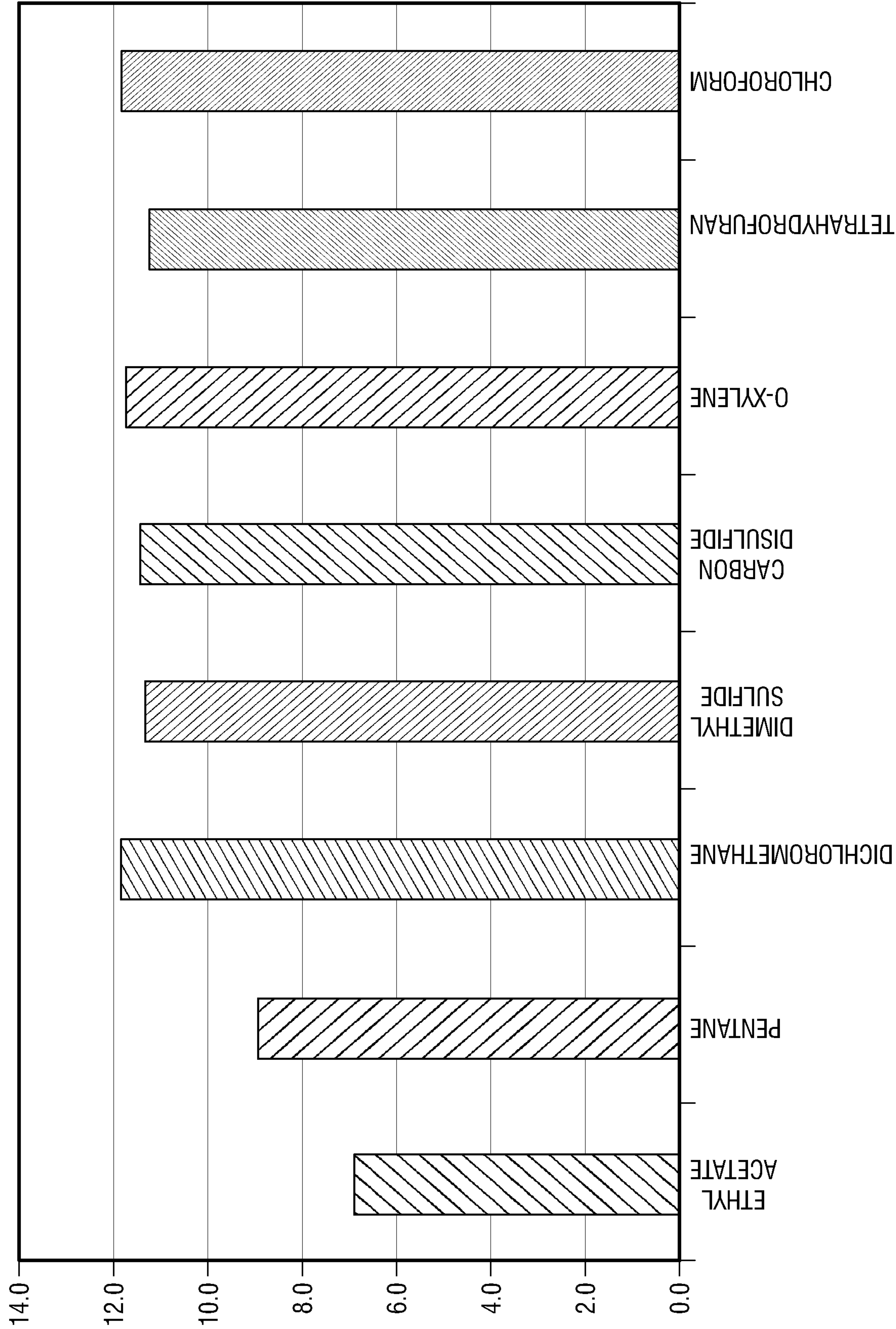
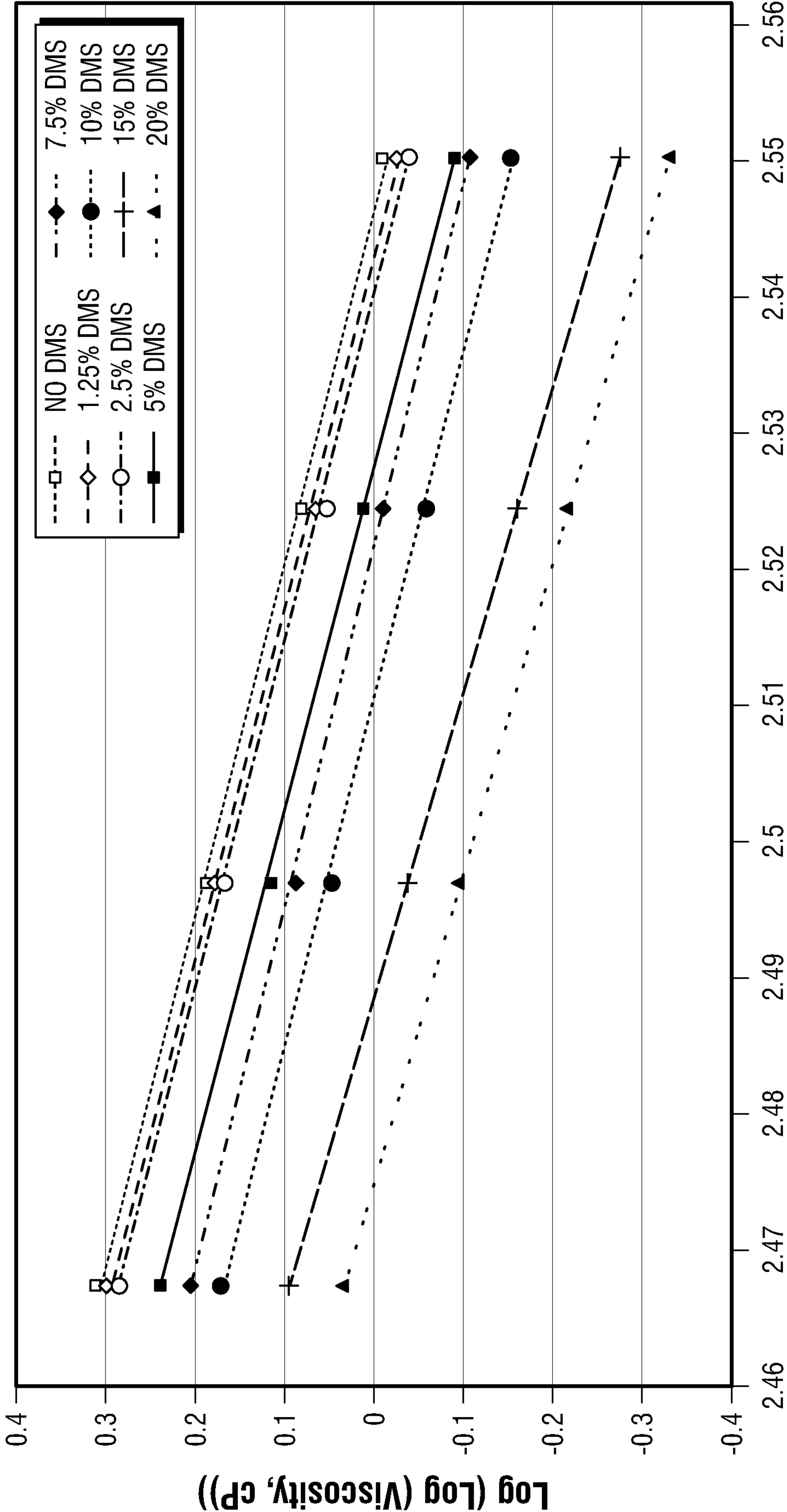


FIG. 7



Log Kelvin

FIG. 8

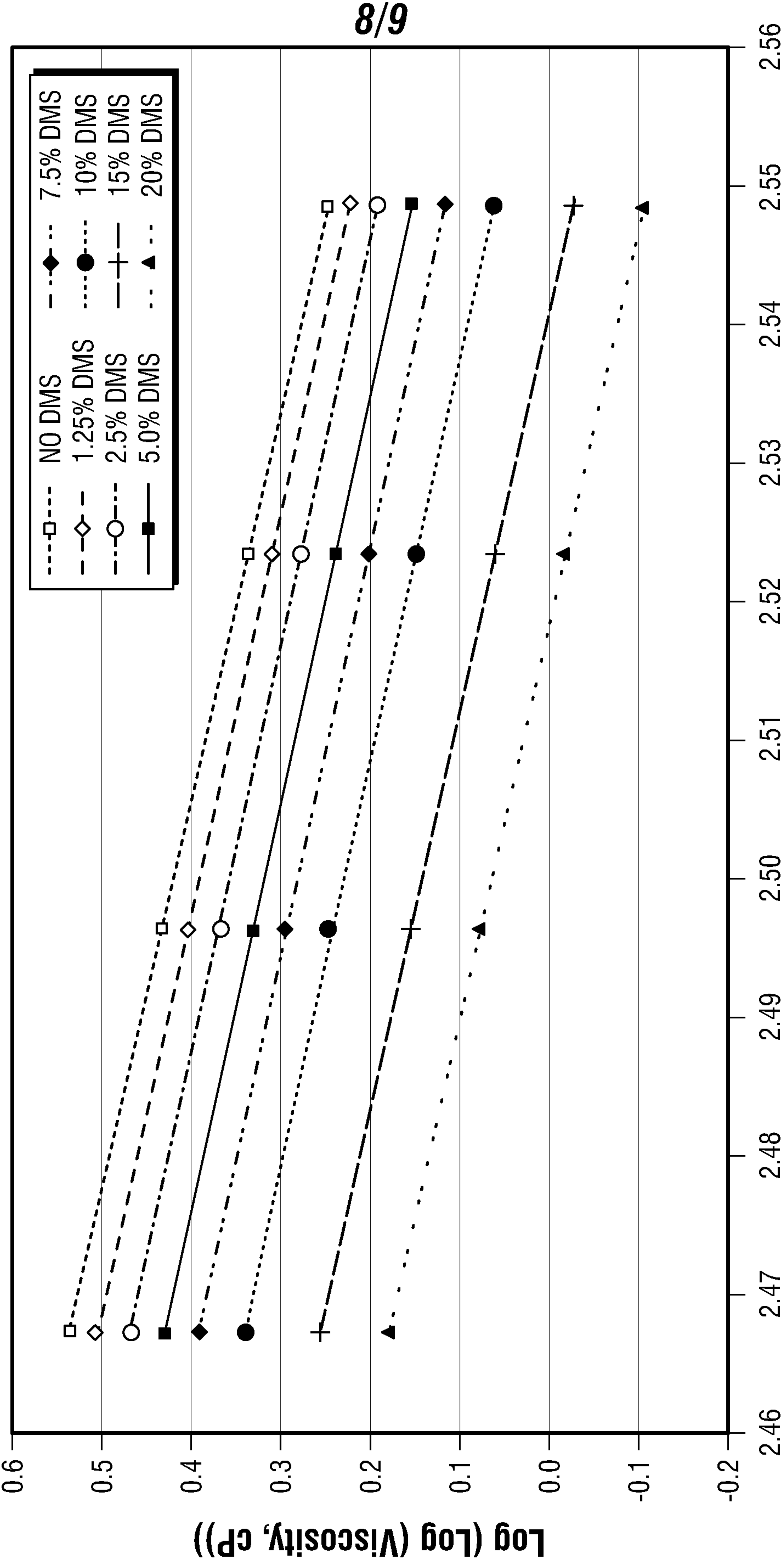
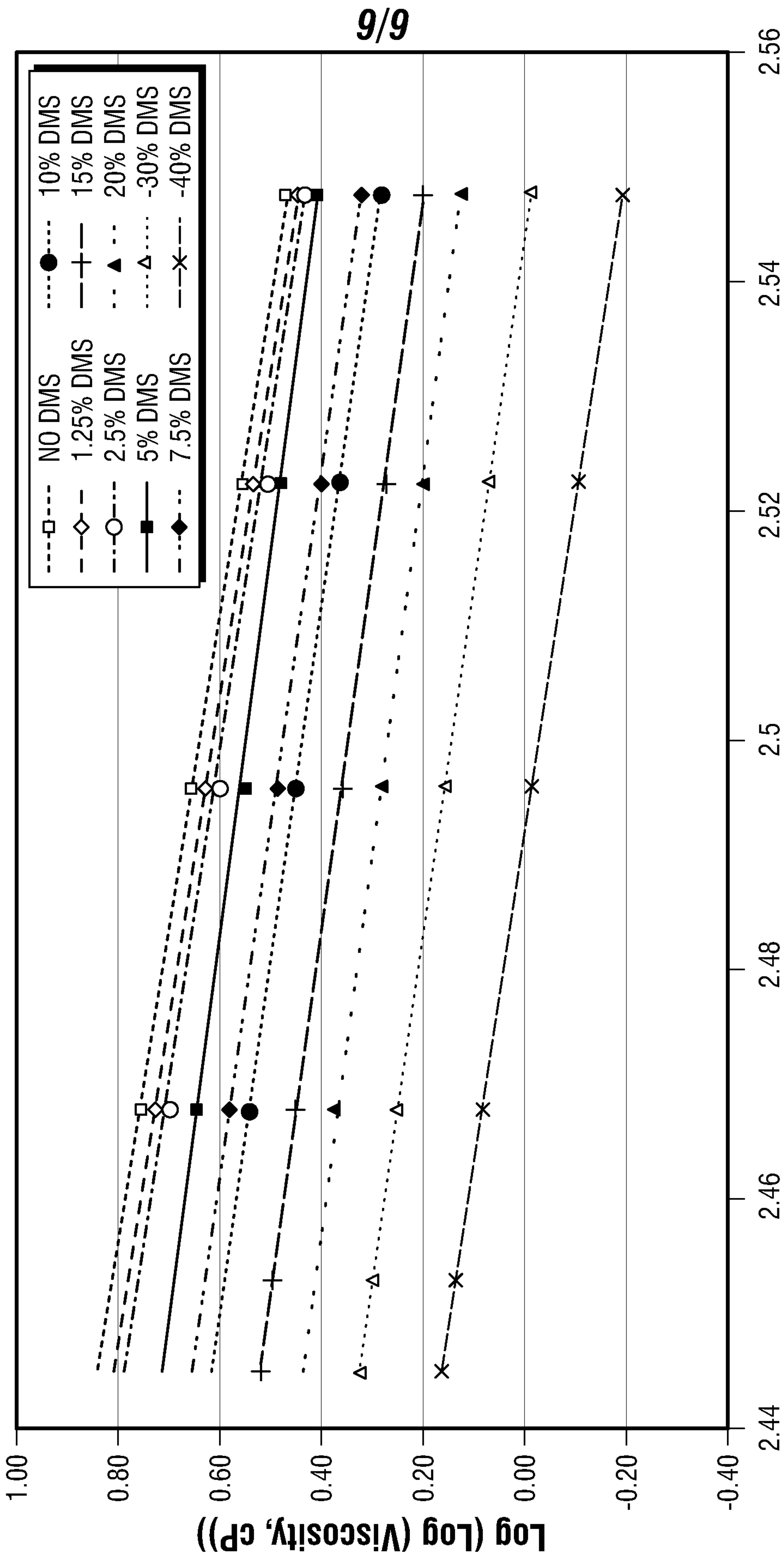


FIG. 9



Log Kelvin
FIG. 10

