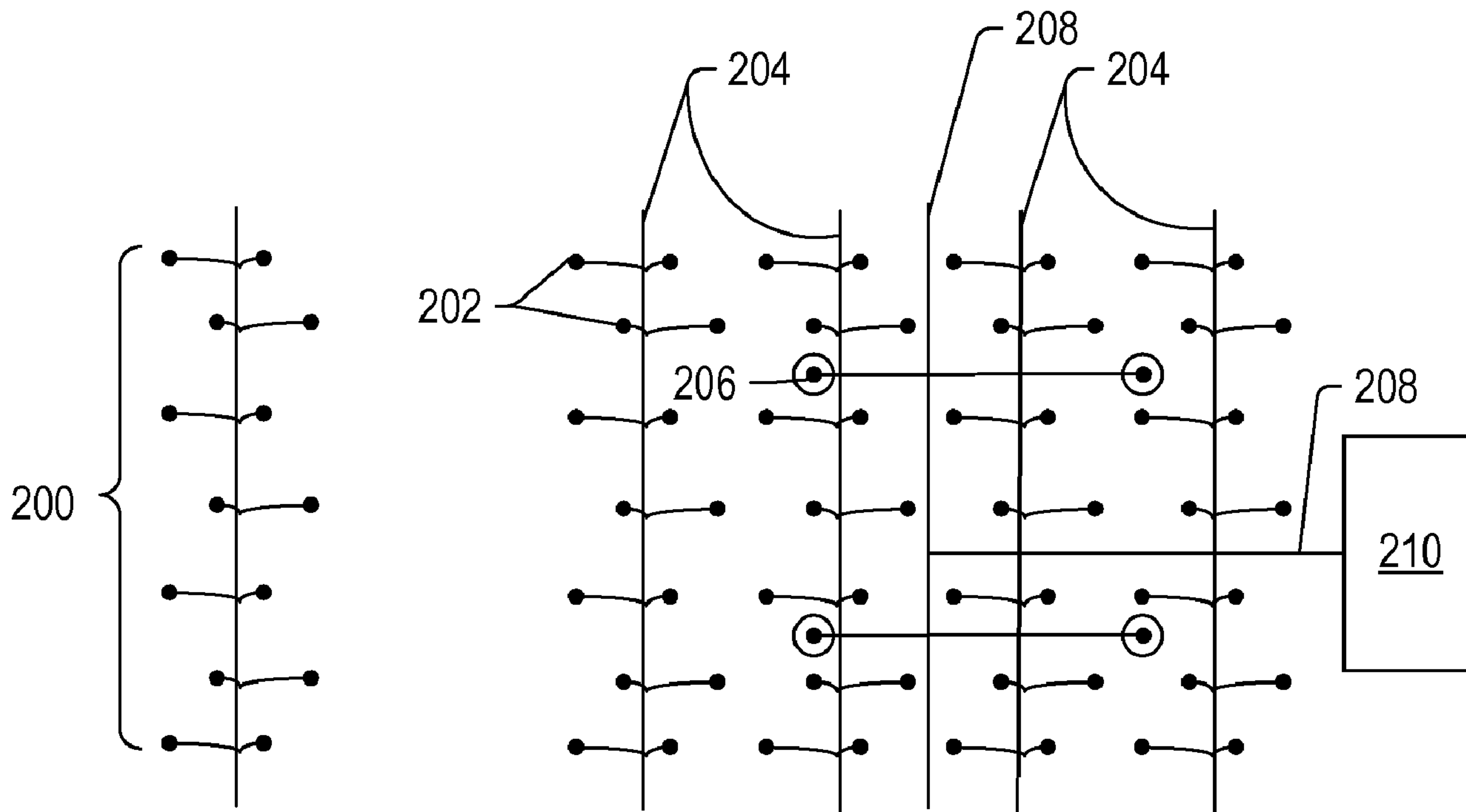




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(57) **Abrégé/Abstract:**

Methods for forming a barrier around at least a portion of a treatment area in a subsurface formation are described herein. Sulfur may be introduced into one or more wellbores located inside a perimeter of a treatment area in the formation having a permeability of at least 0.1 darcy. At least some of the sulfur is allowed to move towards portions of the formation cooler than the melting point of sulfur to solidify the sulfur in the formation to form the barrier.

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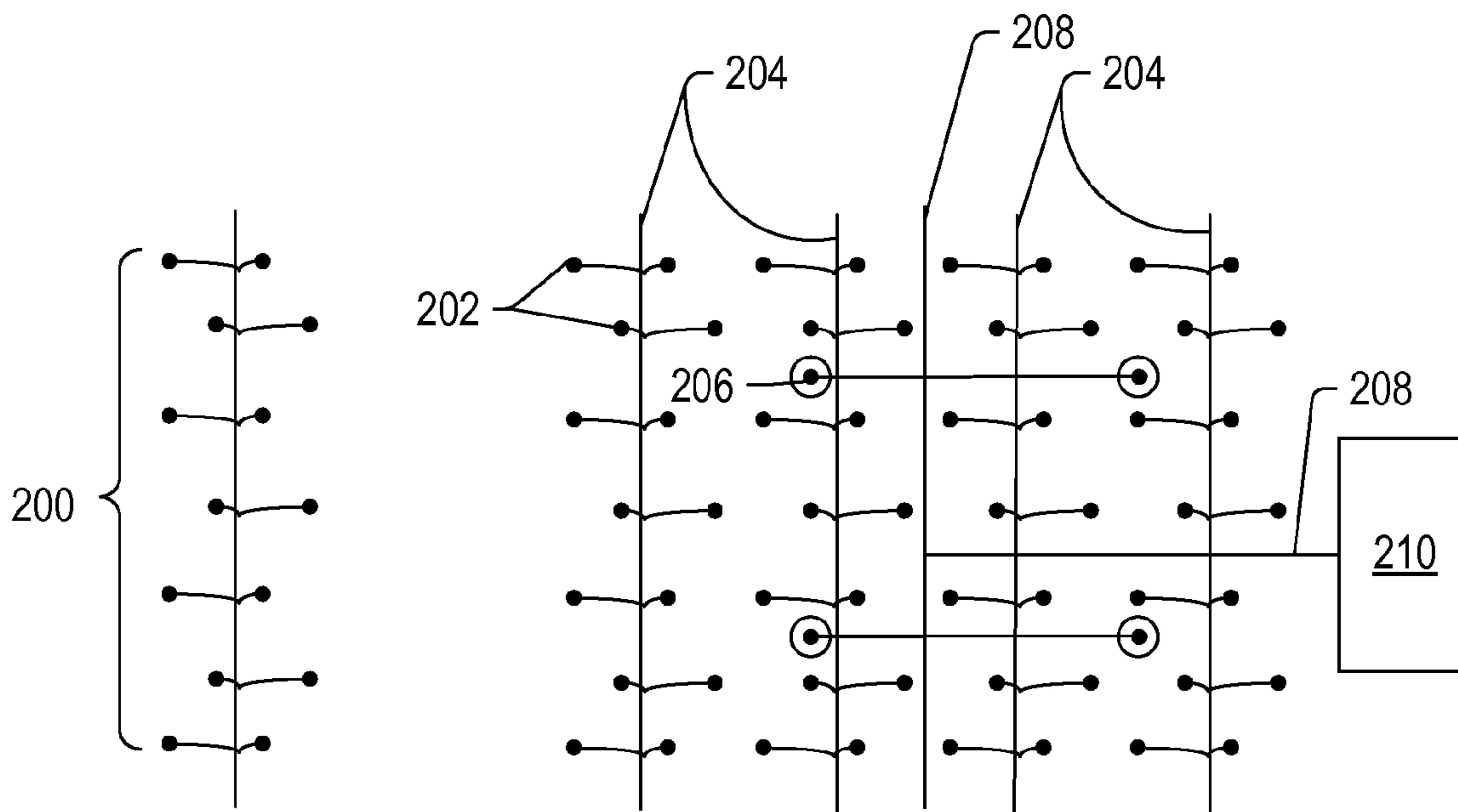
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SULFUR BARRIER FOR USE WITH IN SITU PROCESSES FOR
TREATING FORMATIONS

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GOVERNMENT INTEREST

The U.S. Government has certain rights in this invention pursuant to Agreement No. ERD-05-2516 between UT-Battelle, LLC, operating under prime contract No. DE-ACO5-00OR22725 for the US Department of Energy and Shell Exploration and Production Company.

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BACKGROUND

1. **Field of the Invention**

The present invention relates generally to methods and systems for providing a barrier around at least a portion of a subsurface treatment area. More particularly, the present invention relates to a method of forming a barrier around a treatment area using sulfur. The treatment area may be a treatment area that has been treated by an in situ heat treatment process, is being treated by an in situ heat treatment process, or is to be treated by an in situ heat treatment process.

2. **Description of Related Art**

In situ processes may be used to treat subsurface formations. During some in situ processes, fluids may be introduced or generated in the formation. Introduced or generated fluids may need to be contained in a treatment area to minimize or eliminate impact of the in situ process on adjacent areas. During some in situ processes, a barrier may be formed around all or a portion of the treatment area to inhibit fluids from migrating into or out of the treatment area.

A low temperature zone may be used to isolate selected areas of subsurface formation for many purposes. In some systems, ground is frozen to inhibit migration of fluids from a treatment area during soil remediation. U.S. Patent Nos. 4,860,544 to Krieg et al.; 4,974,425 to Krieg et al.; 5,507,149 to Dash et al.; 6,796,139 to Briley et al.; and 6,854,929 to Vinegar et al. describe systems for freezing ground.

To form a low temperature barrier, spaced apart wellbores may be formed in the formation where the barrier is to be formed. Piping may be placed in the wellbores. A low temperature heat transfer fluid may be circulated through the piping to reduce the temperature adjacent to the wellbores. The low temperature zone around the wellbores may expand outward. Eventually the low temperature zones produced by two adjacent wellbores merge. The temperature of the low temperature zones may be sufficiently low to freeze formation fluid so that a substantially impermeable barrier is formed. The wellbore spacing may be from 1 meter to 3 meter or more. The low temperature barrier may be a significant distance away from a portion of the formation to be heated during using an in situ thermal process.

During in situ processing of some formations, hydrogen sulfide or other sulfur containing compounds may be produced from the formation. In some operations, elemental sulfur may be produced from the sulfur compounds. The sulfur may be produced using a Claus process. The Claus process may result in the production of gas phase sulfur.

5 Forming a low temperature barrier may be a significant investment in equipment, energy and time. Also, after completion of the in situ heat treatment process, keeping the in situ treatment area isolated from surrounding treated or untreated portions of the formation may be desirable. Therefore, it is desirable to be able to form a barrier in the formation from material available at the site of the in situ treatment process that will remain in the formation after in situ process operations
10 are completed.

SUMMARY

Embodiments described herein generally relate to systems, and methods providing a sulfur barrier around at least a portion of a subsurface treatment area.

15 In some embodiments, a method for forming a barrier around at least a portion of a treatment area in a subsurface formation includes introducing sulfur into one or more wellbores located inside a perimeter of a treatment area in the formation; and allowing at least some of the sulfur to move towards portions of the formation cooler than the melting point of sulfur to solidify the sulfur in the formation to form a barrier.

20 In some embodiments, in combination with other embodiments, the treatment area may have a permeability of at least 0.1 darcy, at least 1 darcy, at least 10 darcy, at least 100 darcy.

In some embodiments, in combination with other embodiments the permeability of the treatment has been increased by a solution mining process and/or by an in situ heat treatment process.

25 In some embodiments, in combination with other embodiments, the sulfur is provided as a liquid and/or a vapor into the formation. In some embodiments, in combination with other embodiments, the flow of sulfur is directed towards the perimeter of the treatment area. In some embodiments, in combination with other embodiments, the wellbores through which sulfur is introduced into the formation are located near the perimeter of the treatment area. In some
30 embodiments, in combination with other embodiments, a low temperature barrier at least partially surrounding the treatment area enhances the solidification of the sulfur to form the barrier.

In some embodiments, a method of forming a barrier in a formation includes heating a portion of a formation adjacent to a plurality of wellbores to raise a temperature of the formation adjacent to the wellbores above a melting temperature of sulfur and below a pyrolysis temperature
35 of hydrocarbons in the formation, introducing molten sulfur into at least some of the wellbores; and

allowing the sulfur to move outwards from the wellbores towards portions of the formation cooler than the melting temperature of sulfur so that the sulfur solidifies in the formation to form a barrier.

In some embodiments, in combination with other embodiments, at least one heater used to heat the portion of the formation adjacent the wellbores comprises a temperature limited heater. In some embodiments, in combination with other embodiments, a treatment area inside the barrier is solution mined and/or an in situ heat treatment process is used on a treatment area inside the barrier. In some embodiments, in combination with other embodiments, the barrier is formed between a first barrier and a treatment area used to produce formation fluid from the formation. In some embodiments, in combination with other embodiments, a temperature of the molten sulfur introduced into the formation is near the melting temperature of sulfur. In some embodiments, in combination with other embodiments, carbon dioxide is stored in the treatment area.

In further embodiments, features from specific embodiments may be combined with features from other embodiments. For example, features from one embodiment may be combined with features from any of the other embodiments.

In further embodiments, treating a subsurface formation is performed using any of the methods or systems described herein.

In further embodiments, additional features may be added to the specific embodiments described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

Advantages of the present invention may become apparent to those skilled in the art with the benefit of the following detailed description and upon reference to the accompanying drawings in which:

FIG. 1 depicts an illustration of stages of heating a hydrocarbon containing formation.

FIG. 2 shows a schematic view of an embodiment of a portion of an in situ heat treatment system for treating a hydrocarbon containing formation.

While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are shown by way of example in the drawings and may herein be described in detail. The drawings may not be to scale. It should be understood, however, that the drawings and detailed description thereto are not intended to limit the invention to the particular form disclosed, but on the contrary, the intention is to cover all modifications, equivalents and alternatives falling within the spirit and scope of the present invention as defined by the appended claims.

DETAILED DESCRIPTION

The following description generally relates to systems and methods for treating hydrocarbons in formations. Formations may be treated using in situ conversion processes to yield

hydrocarbon products, hydrogen, and other products. A barrier or barriers may be formed around all or a portion of a treatment area subjected to an in situ heat treatment process.

“Curie temperature” is the temperature above which a ferromagnetic material loses all of its ferromagnetic properties. In addition to losing all of its ferromagnetic properties above the Curie temperature, the ferromagnetic material begins to lose its ferromagnetic properties when an increasing electrical current is passed through the ferromagnetic material.

A “formation” includes one or more hydrocarbon containing layers, one or more non-hydrocarbon layers, an overburden, and/or an underburden. “Hydrocarbon layers” refer to layers in the formation that contain hydrocarbons. The hydrocarbon layers may contain non-hydrocarbon material and hydrocarbon material. The “overburden” and/or the “underburden” include one or more different types of impermeable materials. For example, the overburden and/or underburden may include rock, shale, mudstone, or wet/tight carbonate. In some embodiments of in situ heat treatment processes, the overburden and/or the underburden may include a hydrocarbon containing layer or hydrocarbon containing layers that are relatively impermeable and are not subjected to temperatures during in situ heat treatment processing that result in significant characteristic changes of the hydrocarbon containing layers of the overburden and/or the underburden. For example, the underburden may contain shale or mudstone, but the underburden is not allowed to heat to pyrolysis temperatures during the in situ heat treatment process. In some cases, the overburden and/or the underburden may be somewhat permeable.

“Formation fluids” refer to fluids present in a formation and may include pyrolyzation fluid, synthesis gas, mobilized hydrocarbon, and water (steam). Formation fluids may include hydrocarbon fluids as well as non-hydrocarbon fluids. The term “mobilized fluid” refers to fluids in a hydrocarbon containing formation that are able to flow as a result of thermal treatment of the formation. “Produced fluids” refer to fluids removed from the formation.

A “heat source” is any system for providing heat to at least a portion of a formation substantially by conductive and/or radiative heat transfer. For example, a heat source may include electric heaters such as an insulated conductor, an elongated member, and/or a conductor disposed in a conduit. A heat source may also include systems that generate heat by burning a fuel external to or in a formation. The systems may be surface burners, downhole gas burners, flameless distributed combustors, and natural distributed combustors. In some embodiments, heat provided to or generated in one or more heat sources may be supplied by other sources of energy. The other sources of energy may directly heat a formation, or the energy may be applied to a transfer medium that directly or indirectly heats the formation. It is to be understood that one or more heat sources that are applying heat to a formation may use different sources of energy. Thus, for example, for a given formation some heat sources may supply heat from electric resistance heaters, some heat sources may provide heat from combustion, and some heat sources may provide heat from one or

more other energy sources (for example, chemical reactions, solar energy, wind energy, biomass, or other sources of renewable energy). A chemical reaction may include an exothermic reaction (for example, an oxidation reaction). A heat source may also include a heater that provides heat to a zone proximate and/or surrounding a heating location such as a heater well.

- 5 A “heater” is any system or heat source for generating heat in a well or a near wellbore region. Heaters may be, but are not limited to, electric heaters, burners, combustors that react with material in or produced from a formation, and/or combinations thereof.

“Hydrocarbons” are generally defined as molecules formed primarily by carbon and hydrogen atoms. Hydrocarbons may also include other elements such as, but not limited to, halogens, metallic elements, nitrogen, oxygen, and/or sulfur. Hydrocarbons may be, but are not limited to, kerogen, bitumen, pyrobitumen, oils, natural mineral waxes, and asphaltites. Hydrocarbons may be located in or adjacent to mineral matrices in the earth. Matrices may include, but are not limited to, sedimentary rock, sands, silicilytes, carbonates, diatomites, and other porous media. “Hydrocarbon fluids” are fluids that include hydrocarbons. Hydrocarbon fluids may include, entrain, or be entrained in non-hydrocarbon fluids such as hydrogen, nitrogen, carbon monoxide, carbon dioxide, hydrogen sulfide, water, and ammonia.

An “in situ conversion process” refers to a process of heating a hydrocarbon containing formation from heat sources to raise the temperature of at least a portion of the formation above a pyrolysis temperature so that pyrolyzation fluid is produced in the formation.

20 An “in situ heat treatment process” refers to a process of heating a hydrocarbon containing formation with heat sources to raise the temperature of at least a portion of the formation above a temperature that results in mobilized fluid, visbreaking, and/or pyrolysis of hydrocarbon containing material so that mobilized fluids, visbroken fluids, and/or pyrolyzation fluids are produced in the formation.

25 “Pyrolysis” is the breaking of chemical bonds due to the application of heat. For example, pyrolysis may include transforming a compound into one or more other substances by heat alone. Heat may be transferred to a section of the formation to cause pyrolysis. In some formations, portions of the formation and/or other materials in the formation may promote pyrolysis through catalytic activity.

30 “Temperature limited heater” generally refers to a heater that regulates heat output (for example, reduces heat output) above a specified temperature without the use of external controls such as temperature controllers, power regulators, rectifiers, or other devices. Temperature limited heaters may be AC (alternating current) or modulated (for example, “chopped”) DC (direct current) powered electrical resistance heaters.

“Thermal conductivity” is a property of a material that describes the rate at which heat flows, in steady state, between two surfaces of the material for a given temperature difference between the two surfaces.

5 The term “wellbore” refers to a hole in a formation made by drilling or insertion of a conduit into the formation. A wellbore may have a substantially circular cross section, or another cross-sectional shape. As used herein, the terms “well” and “opening,” when referring to an opening in the formation may be used interchangeably with the term “wellbore.”

10 Some hydrocarbon containing formations, such as oil shale formations, may include nahcolite, trona, and/or other minerals within the formation. In some embodiments, some of the minerals may be recovered from the formation before an in situ heat treatment process is used to produce hydrocarbons and other compounds from the formation.

15 A perimeter barrier may be formed around the portion of the formation to be solution mined to define the treatment area. The perimeter barrier may inhibit migration of water into the treatment area. During solution mining and/or the in situ heat treatment process, the perimeter barrier may inhibit migration of dissolved minerals and formation fluid from the treatment area. The treatment area may be heated using heat sources. During initial heating, a portion of the formation to be treated may be raised to a temperature below the dissociation temperature of the minerals to be recovered. The temperature may be any temperature that increases the solvation rate of the minerals in water, but is also below a temperature at which dissociation occurs (above 95 °C
20 at atmospheric pressure for nahcolite).

A first fluid may be injected into the heated portion. The first fluid may include water, brine, steam, or other fluids that form a solution with the minerals nahcolite. The first fluid may be at an increased temperature, for example, 90 °C, 95 °C, or 100 °C. The increased temperature may be similar to the temperature of the portion of the formation.

25 In some embodiments, the first fluid is injected at an increased temperature into a portion of the formation that has not been heated by heat sources. The increased temperature may be a temperature below a boiling point of the first fluid, for example, 90 °C for water. Providing the first fluid at an increased temperature increases a temperature of a portion of the formation. In certain embodiments, additional heat may be provided from one or more heat sources in the
30 formation during and/or after injection of the first fluid.

In some embodiments, the first fluid is or includes steam. The steam may be produced by forming steam in a previously heated portion of the formation (for example, by passing water through u-shaped wellbores that have been used to heat the formation), by heat exchange with fluids produced from the formation, and/or by generating steam in standard steam production
35 facilities. In some embodiments, the first fluid may be fluid introduced directly into a hot portion

of the portion and produced from the hot portion of the formation. The first fluid may then be used as the first fluid for solution mining.

In some embodiments, heat from a hot previously treated portion of the formation is used to heat water, brine, and/or steam used for solution mining a new portion of the formation. Heat transfer fluid may be introduced into the hot previously treated portion of the formation. The heat transfer fluid may be water, steam, carbon dioxide, and/or other fluids. Heat may transfer from the hot formation to the heat transfer fluid. The heat transfer fluid is produced from the formation through production wells. The heat transfer fluid is sent to a heat exchanger. The heat exchanger may heat water, brine, and/or steam used as the first fluid to solution mine the new portion of the formation. The heat transfer fluid may be reintroduced into the heated portion of the formation to produce additional hot heat transfer fluid. In some embodiments, heat transfer fluid produced from the formation is treated to remove hydrocarbons or other materials before being reintroduced into the formation as part of a remediation process for the heated portion of the formation.

Steam injected for solution mining may have a temperature below the pyrolysis temperature of hydrocarbons in the formation. Injected steam may be at a temperature below 250 °C, below 300 °C, or below 400 °C. The injected steam may be at a temperature of at least 150 °C, at least 135 °C, or at least 125 °C. Injecting steam at pyrolysis temperatures may cause problems as hydrocarbons pyrolyze and hydrocarbon fines mix with the steam. The mixture of fines and steam may reduce permeability and/or cause plugging of production wells and the formation. Thus, the injected steam temperature is selected to inhibit plugging of the formation and/or wells in the formation.

The temperature of the first fluid may be varied during the solution mining process. As the solution mining progresses and the mineral being solution mined is farther away from the injection point, the first fluid temperature may be increased so that steam and/or water that reaches the mineral to be solution mined is at an elevated temperature below the dissociation temperature of the nahcolite. The steam and/or water that reaches the mineral is also at a temperature below a temperature that promotes plugging of the formation and/or wells in the formation (for example, the pyrolysis temperature of hydrocarbons in the formation).

A second fluid may be produced from the formation following injection of the first fluid into the formation. The second fluid may include material dissolved in the first fluid. For example, the second fluid may include carbonic acid or other hydrated carbonate compounds formed from the dissolution of the mineral in the first fluid. The second fluid may also include minerals and/or metals. The minerals and/or metals may include sodium, aluminum, phosphorus, and other elements.

Solution mining the formation before the in situ heat treatment process allows initial heating of the formation to be provided by heat transfer from the first fluid used during solution

mining. Solution mining nahcolite or other minerals that decompose or dissociate by means of endothermic reactions before the in situ heat treatment process avoids having energy supplied to heat the formation being used to support these endothermic reactions. Solution mining allows for production of minerals with commercial value. Removing nahcolite or other minerals before the in situ heat treatment process removes mass from the formation. Thus, less mass is present in the formation that needs to be heated to higher temperatures and heating the formation to higher temperatures may be achieved more quickly and/or more efficiently. Removing mass from the formation also may increase the permeability of the formation. Increasing the permeability may reduce the number of production wells needed for the in situ heat treatment process. In certain embodiments, solution mining before the in situ heat treatment process reduces the time delay between startup of heating of the formation and production of hydrocarbons by two years or more.

Hydrocarbons in formations may be treated in various ways to produce many different products. In certain embodiments, hydrocarbons in formations are treated in stages. FIG. 1 depicts an illustration of stages of heating the hydrocarbon containing formation. FIG. 1 also depicts an example of yield ("Y") in barrels of oil equivalent per ton (y axis) of formation fluids from the formation versus temperature ("T") of the heated formation in degrees Celsius (x axis).

Desorption of methane and vaporization of water occurs during stage 1 heating. Heating of the formation through stage 1 may be performed as quickly as possible. For example, when the hydrocarbon containing formation is initially heated, hydrocarbons in the formation desorb adsorbed methane. The desorbed methane may be produced from the formation. If the hydrocarbon containing formation is heated further, water in the hydrocarbon containing formation is vaporized. Water may occupy, in some hydrocarbon containing formations, between 10% and 50% of the pore volume in the formation. In other formations, water occupies larger or smaller portions of the pore volume. Water typically is vaporized in a formation between 160 °C and 285 °C at pressures of 600 kPa absolute to 7000 kPa absolute. In some embodiments, the vaporized water produces wettability changes in the formation and/or increased formation pressure. The wettability changes and/or increased pressure may affect pyrolysis reactions or other reactions in the formation. In certain embodiments, the vaporized water is produced from the formation. In other embodiments, the vaporized water is used for steam extraction and/or distillation in the formation or outside the formation. Removing the water from and increasing the pore volume in the formation increases the storage space for hydrocarbons in the pore volume.

In certain embodiments, after stage 1 heating, the formation is heated further, such that a temperature in the formation reaches (at least) an initial pyrolyzation temperature (such as a temperature at the lower end of the temperature range shown as stage 2). Hydrocarbons in the formation may be pyrolyzed throughout stage 2. A pyrolysis temperature range varies depending on the types of hydrocarbons in the formation. The pyrolysis temperature range may include

temperatures between 250 °C and 900 °C. The pyrolysis temperature range for producing desired products may extend through only a portion of the total pyrolysis temperature range. In some embodiments, the pyrolysis temperature range for producing desired products may include temperatures between 250 °C and 400 °C or temperatures between 270 °C and 350 °C. If a
5 temperature of hydrocarbons in the formation is slowly raised through the temperature range from 250 °C to 400 °C, production of pyrolysis products may be substantially complete when the temperature approaches 400 °C. Average temperature of the hydrocarbons may be raised at a rate of less than 5 °C per day, less than 2 °C per day, less than 1 °C per day, or less than 0.5 °C per day through the pyrolysis temperature range for producing desired products. Heating the hydrocarbon
10 containing formation with a plurality of heat sources may establish thermal gradients around the heat sources that slowly raise the temperature of hydrocarbons in the formation through the pyrolysis temperature range.

The rate of temperature increase through the pyrolysis temperature range for desired products may affect the quality and quantity of the formation fluids produced from the hydrocarbon
15 containing formation. Raising the temperature slowly through the pyrolysis temperature range for desired products may inhibit mobilization of large chain molecules in the formation. Raising the temperature slowly through the pyrolysis temperature range for desired products may limit reactions between mobilized hydrocarbons that produce undesired products. Slowly raising the temperature of the formation through the pyrolysis temperature range for desired products may
20 allow for the production of high quality, high API gravity hydrocarbons from the formation. Slowly raising the temperature of the formation through the pyrolysis temperature range for desired products may allow for the removal of a large amount of the hydrocarbons present in the formation as hydrocarbon product.

In some in situ heat treatment embodiments, a portion of the formation is heated to a
25 desired temperature instead of slowly heating the temperature through a temperature range. In some embodiments, the desired temperature is 300 °C, 325 °C, or 350 °C. Other temperatures may be selected as the desired temperature. Superposition of heat from heat sources allows the desired temperature to be relatively quickly and efficiently established in the formation. Energy input into the formation from the heat sources may be adjusted to maintain the temperature in the formation
30 substantially at the desired temperature. The heated portion of the formation is maintained substantially at the desired temperature until pyrolysis declines such that production of desired formation fluids from the formation becomes uneconomical. Parts of the formation that are subjected to pyrolysis may include regions brought into a pyrolysis temperature range by heat transfer from only one heat source.

35 In certain embodiments, formation fluids including pyrolyzation fluids are produced from the formation. As the temperature of the formation increases, the amount of condensable

hydrocarbons in the produced formation fluid may decrease. At high temperatures, the formation may produce mostly methane and/or hydrogen. If the hydrocarbon containing formation is heated throughout an entire pyrolysis range, the formation may produce only small amounts of hydrogen towards an upper limit of the pyrolysis range. After all of the available hydrogen is depleted, a
5 minimal amount of fluid production from the formation will typically occur.

After pyrolysis of hydrocarbons, a large amount of carbon and some hydrogen may still be present in the formation. A significant portion of carbon remaining in the formation can be produced from the formation in the form of synthesis gas. Synthesis gas generation may take place during stage 3 heating depicted in FIG. 1. Stage 3 may include heating a hydrocarbon containing
10 formation to a temperature sufficient to allow synthesis gas generation. For example, synthesis gas may be produced in a temperature range from 400 °C to 1200 °C, 500 °C to 1100 °C, or 550 °C to 1000 °C. The temperature of the heated portion of the formation when the synthesis gas generating fluid is introduced to the formation determines the composition of synthesis gas produced in the formation. The generated synthesis gas may be removed from the formation through a production
15 well or production wells.

Total energy content of fluids produced from the hydrocarbon containing formation may stay relatively constant throughout pyrolysis and synthesis gas generation. During pyrolysis at relatively low formation temperatures, a significant portion of the produced fluid may be condensable hydrocarbons that have a high energy content. At higher pyrolysis temperatures,
20 however, less of the formation fluid may include condensable hydrocarbons. More non-condensable formation fluids may be produced from the formation. Energy content per unit volume of the produced fluid may decline slightly during generation of predominantly non-condensable formation fluids. During synthesis gas generation, energy content per unit volume of produced synthesis gas declines significantly compared to energy content of pyrolyzation fluid.
25 The volume of the produced synthesis gas, however, will in many instances increase substantially, thereby compensating for the decreased energy content.

FIG. 2 depicts a schematic view of an embodiment of a portion of the in situ heat treatment system for treating the hydrocarbon containing formation. The in situ heat treatment system may include barrier wells 200. Barrier wells are used to form a barrier around a treatment area. The
30 barrier inhibits fluid flow into and/or out of the treatment area. Barrier wells include, but are not limited to, dewatering wells, vacuum wells, capture wells, injection wells, grout wells, freeze wells, or combinations thereof. In some embodiments, barrier wells 200 are dewatering wells. Dewatering wells may remove liquid water and/or inhibit liquid water from entering a portion of the formation to be heated, or to the formation being heated.

Freeze wells may be used to establish a low temperature zone around all or a portion of a
35 treatment area. Refrigerant is circulated through freeze wells to form low temperature zones

around each freeze well. The freeze wells are placed in the formation so that the low temperature zones overlap and form a low temperature zone around the treatment area. The low temperature zone established by freeze wells is maintained below the freezing temperature of aqueous fluid in the formation. Aqueous fluid entering the low temperature zone freezes and forms a frozen barrier.

5 In the embodiment depicted in FIG. 2, the barrier wells 200 are shown extending only along one side of heat sources 202, but the barrier wells typically encircle all heat sources 202 used, or to be used, to heat a treatment area of the formation.

Heat sources 202 are placed in at least a portion of the formation. Heat sources 202 may include heaters such as insulated conductors, conductor-in-conduit heaters, surface burners,
10 flameless distributed combustors, and/or natural distributed combustors. Heat sources 202 may also include other types of heaters. Heat sources 202 provide heat to at least a portion of the formation to heat hydrocarbons in the formation. Energy may be supplied to heat sources 202 through supply lines 204. Supply lines 204 may be structurally different depending on the type of heat source or heat sources used to heat the formation. Supply lines 204 for heat sources may
15 transmit electricity for electric heaters, may transport fuel for combustors, or may transport heat exchange fluid that is circulated in the formation. In some embodiments, electricity for an in situ heat treatment process may be provided by a nuclear power plant or nuclear power plants. The use of nuclear power may allow for reduction or elimination of carbon dioxide emissions from the in situ heat treatment process.

20 Production wells 206 are used to remove formation fluid from the formation. In some embodiments, production well 206 includes a heat source. The heat source in the production well may heat one or more portions of the formation at or near the production well. In some in situ heat treatment process embodiments, the amount of heat supplied to the formation from the production well per meter of the production well is less than the amount of heat applied to the formation from
25 a heat source that heats the formation per meter of the heat source. Heat applied to the formation from the production well may increase formation permeability adjacent to the production well by vaporizing and removing liquid phase fluid adjacent to the production well and/or by increasing the permeability of the formation adjacent to the production well by formation of macro and/or micro fractures.

30 In some embodiments, the heat source in production well 206 allows for vapor phase removal of formation fluids from the formation. Providing heating at or through the production well may: (1) inhibit condensation and/or refluxing of production fluid when such production fluid is moving in the production well proximate the overburden, (2) increase heat input into the formation, (3) increase production rate from the production well as compared to a production well
35 without a heat source, (4) inhibit condensation of high carbon number compounds (C6 and above)

in the production well, and/or (5) increase formation permeability at or proximate the production well.

Subsurface pressure in the formation may correspond to the fluid pressure generated in the formation. As temperatures in the heated portion of the formation increase, the pressure in the heated portion may increase as a result of increased fluid generation and vaporization of water. Controlling rate of fluid removal from the formation may allow for control of pressure in the formation. Pressure in the formation may be determined at a number of different locations, such as near or at production wells, near or at heat sources, or at monitor wells.

In some hydrocarbon containing formations, production of hydrocarbons from the formation is inhibited until at least some hydrocarbons in the formation have been pyrolyzed. Formation fluid may be produced from the formation when the formation fluid is of a selected quality. In some embodiments, the selected quality includes an API gravity of at least 20°, 30°, or 40°. Inhibiting production until at least some hydrocarbons are pyrolyzed may increase conversion of heavy hydrocarbons to light hydrocarbons. Inhibiting initial production may minimize the production of heavy hydrocarbons from the formation. Production of substantial amounts of heavy hydrocarbons may require expensive equipment and/or reduce the life of production equipment.

After pyrolysis temperatures are reached and production from the formation is allowed, pressure in the formation may be varied to alter and/or control a composition of formation fluid produced, to control a percentage of condensable fluid as compared to non-condensable fluid in the formation fluid, and/or to control an API gravity of formation fluid being produced. For example, decreasing pressure may result in production of a larger condensable fluid component. The condensable fluid component may contain a larger percentage of olefins.

In some in situ heat treatment process embodiments, pressure in the formation may be maintained high enough to promote production of formation fluid with an API gravity of greater than 20°. Maintaining increased pressure in the formation may inhibit formation subsidence during in situ heat treatment. Maintaining increased pressure may facilitate vapor phase production of fluids from the formation. Vapor phase production may allow for a reduction in size of collection conduits used to transport fluids produced from the formation. Maintaining increased pressure may reduce or eliminate the need to compress formation fluids at the surface to transport the fluids in collection conduits to treatment facilities.

Maintaining increased pressure in a heated portion of the formation may surprisingly allow for production of large quantities of hydrocarbons of increased quality and of relatively low molecular weight. Pressure may be maintained so that formation fluid produced has a minimal amount of compounds above a selected carbon number. The selected carbon number may be at most 25, at most 20, at most 12, or at most 8. Some high carbon number compounds may be entrained in vapor in the formation and may be removed from the formation with the vapor.

Maintaining increased pressure in the formation may inhibit entrainment of high carbon number compounds and/or multi-ring hydrocarbon compounds in the vapor. High carbon number compounds and/or multi-ring hydrocarbon compounds may remain in a liquid phase in the formation for significant time periods. The significant time periods may provide sufficient time for the compounds to pyrolyze to form lower carbon number compounds.

Formation fluid produced from production wells 206 may be transported through collection piping 208 to treatment facilities 210. Formation fluids may also be produced from heat sources 202. For example, fluid may be produced from heat sources 202 to control pressure in the formation adjacent to the heat sources. Fluid produced from heat sources 202 may be transported through tubing or piping to collection piping 208 or the produced fluid may be transported through tubing or piping directly to treatment facilities 210. Treatment facilities 210 may include separation units, reaction units, upgrading units, fuel cells, turbines, storage vessels, and/or other systems and units for processing produced formation fluids. The treatment facilities may form transportation fuel from at least a portion of the hydrocarbons produced from the formation. In some embodiments, the transportation fuel may be jet fuel, such as JP-8.

Hydrocarbons or other desired products in a formation may be produced using various in situ processes. Some in situ processes that may be used to produce hydrocarbons or desired products are in situ conversion processes, steam flooding, fire flooding, steam-assisted gravity drainage, and solution mining. During some in situ processes, barriers may be needed or required. Barriers may inhibit fluid, such as formation water, from entering a treatment area. Barriers may also inhibit undesired exit of fluid from the treatment area. Inhibiting undesired exit of fluid from the treatment area may minimize or eliminate impact of the in situ process on areas adjacent to the treatment area.

In some embodiments, the barrier is formed a significant distance away from wells used to heat or otherwise treat a treatment area. The barrier may be formed 10 m, 30 m, 50 m, 100 m or farther away from wells used to heat or otherwise treat a treatment area.

In situ heat treatment processes and solution mining processes may heat the treatment area, remove mass from the treatment area, and greatly increase the permeability of the treatment area. In certain embodiments, the treatment area after being treated may have a permeability of at least 0.1 darcy. In some embodiments, the treatment area after being treated has a permeability of at least 1 darcy, of at least 10 darcy, or of at least 100 darcy. The increased permeability allows the fluid to spread in the formation into fractures, microfractures, and/or pore spaces in the formation. Outside of the treatment area, the permeability may remain at the initial permeability of the formation. The increased permeability allows fluid introduced to flow easily within the formation.

In certain embodiments, a barrier may be formed in the formation after a solution mining process and/or an in situ heat treatment process by introducing a fluid into the formation. The

barrier may inhibit formation fluid from entering the treatment area after the solution mining and/or in situ heat treatment processes have ended. The barrier formed by introducing fluid into the formation may allow for isolation of the treatment area.

The fluid introduced into the formation to form a barrier may include wax, bitumen, heavy oil, sulfur, polymer, gel, saturated saline solution, and/or one or more reactants that react to form a precipitate, solid or high viscosity fluid in the formation. In some embodiments, bitumen, heavy oil, reactants and/or sulfur used to form the barrier are obtained from treatment facilities associated with the in situ heat treatment process. For example, sulfur may be obtained from a Claus process used to treat produced gases to remove hydrogen sulfide and other sulfur compounds.

The fluid may be introduced into the formation as a liquid, vapor, or mixed phase fluid. The fluid may be introduced into a portion of the formation that is at an elevated temperature. In some embodiments, the fluid is introduced into the formation through wells located near a perimeter of the treatment area. The fluid may be directed away from the treatment area. The elevated temperature of the formation maintains or allows the fluid to have a low viscosity so that the fluid moves away from the wells. A portion of the fluid may spread outwards in the formation towards a cooler portion of the formation. The relatively high permeability of the formation allows fluid introduced from one wellbore to spread and mix with fluid introduced from other wellbores. In the cooler portion of the formation, the viscosity of the fluid increases, a portion of the fluid precipitates, and/or the fluid solidifies or thickens so that the fluid forms the barrier to flow of formation fluid into or out of the treatment area.

In some embodiments, a low temperature barrier formed by freeze wells surrounds all or a portion of the treatment area. As the fluid introduced into the formation approaches the low temperature barrier, the temperature of the formation becomes colder. The colder temperature increases the viscosity of the fluid, enhances precipitation, and/or solidifies the fluid to form the barrier to the flow of formation fluid into or out of the formation. The fluid may remain in the formation as a highly viscous fluid or a solid after the low temperature barrier has dissipated.

In certain embodiments, saturated saline solution is introduced into the formation. Components in the saturated saline solution may precipitate out of solution when the solution reaches a colder temperature. The solidified particles may form the barrier to the flow of formation fluid into or out of the formation. The solidified components may be substantially insoluble in formation fluid.

In certain embodiments, brine is introduced into the formation as a reactant. A second reactant, such as carbon dioxide, may be introduced into the formation to react with the brine. The reaction may generate a mineral complex that grows in the formation. The mineral complex may be substantially insoluble to formation fluid. In an embodiment, the brine solution includes a sodium and aluminum solution. The second reactant introduced in the formation is carbon dioxide.

The carbon dioxide reacts with the brine solution to produce dawsonite. The minerals may solidify and form the barrier to the flow of formation fluid into or out of the formation.

In some embodiments, the barrier may be formed around a treatment area using sulfur. Advantageously, elemental sulfur is insoluble in water. Liquid and/or solid sulfur in the formation
5 may form a barrier to formation fluid flow into or out of the treatment area.

A sulfur barrier may be established in the formation during or before initiation of heating to heat the treatment area of the in situ heat treatment process. In some embodiments, sulfur may be introduced into wellbores in the formation that are located between the treatment area and a first barrier (for example, a low temperature barrier established by freeze wells). The formation
10 adjacent to the wellbores that the sulfur is introduced into may be dewatered. In some embodiments, the formation adjacent to the wellbores that the sulfur is introduced into is heated to facilitate removal of water and to prepare the wellbores and adjacent formation for the introduction of sulfur. The formation adjacent to the wellbores may be heated to a temperature below the
15 pyrolysis temperature of hydrocarbons in the formation. The formation may be heated so that the temperature of a portion of the formation between two adjacent heaters is influenced by both heaters. In some embodiments, the heat may increase the permeability of the formation so that a first wellbore is in fluid communication with an adjacent wellbore.

After the formation adjacent to the wellbores is heated, molten sulfur at a temperature below the pyrolysis temperature of hydrocarbons in the formation is introduced into the formation.
20 Over a certain temperature range, the viscosity of molten sulfur increases with increasing temperature. The molten sulfur introduced into the formation may be near the melting temperature of sulfur (115 °C) so that the sulfur has a relatively low viscosity (4-10 cp). Heaters in the wellbores may be temperature limited heaters with Curie temperatures near the melting temperature of sulfur so that the temperature of the molten sulfur stays relatively constant and below
25 temperatures resulting in the formation of viscous molten sulfur. In some embodiments, the region adjacent to the wellbores may be heated to a temperature above the melting point of sulfur, but below the pyrolysis temperature of hydrocarbons in the formation. The heaters may be turned off and the temperature in the wellbores may be monitored (for example, using a fiber optic temperature monitoring system). When the temperature in the wellbore cools to a temperature near
30 the melting temperature of sulfur, molten sulfur may be introduced into the formation.

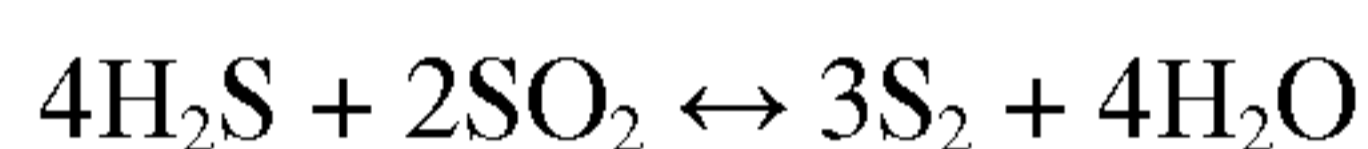
The sulfur introduced into the formation is allowed to flow and diffuse into the formation from the wellbores. As the sulfur enters portions of the formation below the melting temperature, the sulfur solidifies and forms a barrier to fluid flow in the formation. Sulfur may be introduced until the formation is not able to accept additional sulfur. Heating may be stopped, and the
35 formation may be allowed to naturally cool so that the sulfur in the formation solidifies. After

introduction of the sulfur, the integrity of the formed barrier may be tested using pulse tests and/or tracer tests.

A barrier may be formed around the treatment area after the in situ heat treatment process. The sulfur may form a substantially permanent barrier in the formation. In some embodiments, a low temperature barrier formed by freeze wells surrounds the treatment area. Sulfur may be introduced on one or both sides of the low temperature barrier to form a barrier in the formation. The sulfur may be introduced into the formation as vapor or a liquid. As the sulfur approaches the low temperature barrier, the sulfur may condense and/or solidify in the formation to form the barrier.

In some embodiments, the sulfur may be introduced in the heated portion of the portion. The sulfur may be introduced into the formation through wells located near the perimeter of the treatment area. The temperature of the formation may be hotter than the vaporization temperature of sulfur (445 °C). The sulfur may be introduced as a liquid, vapor or mixed phase fluid. If a part of the introduced sulfur is in the liquid phase, the heat of the formation may vaporize the sulfur. The sulfur may flow outwards from the introduction wells towards cooler portions of the formation. The sulfur may condense and/or solidify in the formation to form the barrier.

In some embodiments, the Claus reaction may be used to form sulfur in the formation after the in situ heat treatment process. The Claus reaction is a gas phase equilibrium reaction. The Claus reaction is:



Hydrogen sulfide may be obtained by separating the hydrogen sulfide from the produced fluid of an ongoing in situ heat treatment process. A portion of the hydrogen sulfide may be burned to form the needed sulfur dioxide. Hydrogen sulfide may be introduced into the formation through a number of wells in the formation. Sulfur dioxide may be introduced into the formation through other wells. The wells used for injecting sulfur dioxide or hydrogen sulfide may have been production wells, heater wells, monitor wells or other type of well during the in situ heat treatment process of the treatment area. The wells used for injecting sulfur dioxide or hydrogen sulfide may be near the perimeter of the treatment area. The number of wells may be enough so that the formation in the vicinity of the injection wells does not cool to a point where the sulfur dioxide and the hydrogen sulfide can form sulfur and condense, rather than remain in the vapor phase. In some embodiments, the hydrogen sulfide and sulfur dioxide may be introduced into the formation through the same wells (for example, through two conduits positioned in the same wellbore). The hydrogen sulfide and the sulfur dioxide may react in the formation to form sulfur and water. The

sulfur may flow outwards in the formation and condense and/or solidify to form the barrier in the formation.

The sulfur barrier may form in the formation beyond the area where hydrocarbons in formation fluid generated by the heat treatment process condense in the formation. Regions near
5 the perimeter of the treated area may be at lower temperatures than the treated area. Sulfur may condense and/or solidify from the vapor phase in these lower temperature regions. Additional hydrogen sulfide, and/or sulfur dioxide may diffuse to these lower temperature regions. Additional sulfur may form by the Claus reaction to maintain an equilibrium concentration of sulfur in the vapor phase. Eventually, the sulfur barrier may form around the treated zone. The vapor phase in
10 the treated region may remain as an equilibrium mixture of sulfur, hydrogen sulfide, sulfur dioxide, water vapor. The vapor phase may also include other vapor products present in or evolving from the formation.

The conversion to sulfur is favored at lower temperatures, so the conversion of hydrogen sulfide and sulfur dioxide to sulfur may take place a distance away from the wells that introduce the
15 reactants into the formation. The Claus reaction may result in the formation of sulfur where the temperature of the formation is cooler (for example where the temperature of the formation is at temperatures from about 180 °C to about 240 °C).

Further modifications and alternative embodiments of various aspects of the invention may be apparent to those skilled in the art in view of this description. Accordingly, this description is to
20 be construed as illustrative only and is for the purpose of teaching those skilled in the art the general manner of carrying out the invention. It is to be understood that the forms of the invention shown and described herein are to be taken as the presently preferred embodiments. Elements and materials may be substituted for those illustrated and described herein, parts and processes may be reversed, and certain features of the invention may be utilized independently, all as would be
25 apparent to one skilled in the art after having the benefit of this description of the invention. Changes may be made in the elements described herein without departing from the spirit and scope of the invention as described in the following claims. In addition, it is to be understood that features described herein independently may, in certain embodiments, be combined.

CLAIMS

1. A method for forming a barrier around at least a portion of a treatment area in a subsurface formation, comprising:
 - 5 introducing sulfur into one or more wellbores located inside a perimeter of a treatment area in the formation, wherein the treatment area has a permeability of at least 0.1 darcy; and allowing at least some of the sulfur to move towards portions of the formation cooler than the melting point of sulfur to solidify the sulfur in the formation to form a barrier.
 2. The method as claimed in claim 1, wherein the treatment area has a permeability of at least
10 1 darcy.
 3. The method as claimed in claim,1, wherein the treatment area has a permeability of at least 10 darcy.
 4. The method as claimed in claim 1, wherein the treatment area has a permeability of at least 100 darcy.
 - 15 5. The method as claimed in any of claims 1-4, wherein the permeability of the treatment has been increased by a solution mining process.
 6. The method as claimed in any of claims 1-5, wherein the permeability of the treatment has been increased by an in situ heat treatment process.
 7. The method as claimed in any of claims 1-6, wherein introducing at least a portion of the
20 sulfur into one or more wellbores comprises providing hydrogen sulfide and sulfur dioxide into wellbores, and wherein the hydrogen sulfide and sulfur dioxide react in the formation to produce sulfur.
 8. The method as claimed in any of claims 1-7, wherein at least a portion of the sulfur introduced into the wellbores is in a liquid state.
 - 25 9. The method as claimed in claim 8, wherein the heat of the formation adjacent to the wellbore vaporizes the liquid sulfur.
 10. The method as claimed in any of claims 1-9, wherein at least a portion of the sulfur is introduced into the wellbores is in a vapor phase.
 11. The method as claimed in any of claims 1-10, wherein the flow of sulfur is directed
30 towards the perimeter of the treatment area.
 12. The method as claimed in any of claims 1-11, wherein the wellbores through which sulfur is introduced into the formation are located near the perimeter of the treatment area.
 13. The method as claimed in any of claims 1-12, wherein a low temperature barrier at least partially surrounding the treatment area enhances the solidification of the sulfur to form the barrier.

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14. A method of forming a barrier in a formation, comprising:
heating a portion of a formation adjacent to a plurality of wellbores to raise a temperature
of the formation adjacent to the wellbores above a melting temperature of sulfur and below
a pyrolysis temperature of hydrocarbons in the formation;
- 5 introducing sulfur into the formation from at least some of the wellbores; and
allowing the sulfur to move outwards from the wellbores towards portions of the formation
cooler than the melting temperature of sulfur so that the sulfur solidifies in the formation to
form a barrier.
15. The method as claimed in claim 14, wherein introducing sulfur into the formation
10 comprises providing hydrogen sulfide and sulfur dioxide to the formation such that at least some of
the hydrogen sulfide and sulfur dioxide react in the formation to produce sulfur.
16. The method as claimed in any of claims 14 or 15, wherein at least one heater used to heat
the portion of the formation adjacent the wellbores comprises a temperature limited heater.
17. The method as claimed in any of claims 14-16, further comprising solution mining a
15 treatment area inside the barrier.
18. The method as claimed in any of claims 14-17, further comprising using an in situ heat
treatment process on a treatment area inside the barrier.
19. The method as claimed in any of claims 14-18, further comprising forming the barrier
between a first barrier and a treatment area used to produce formation fluid from the formation.
20. The method as claimed in any of claims 14-19, wherein introducing sulfur into the
20 formation comprises injecting molten sulfur into the formation through at least some of the
wellbores.

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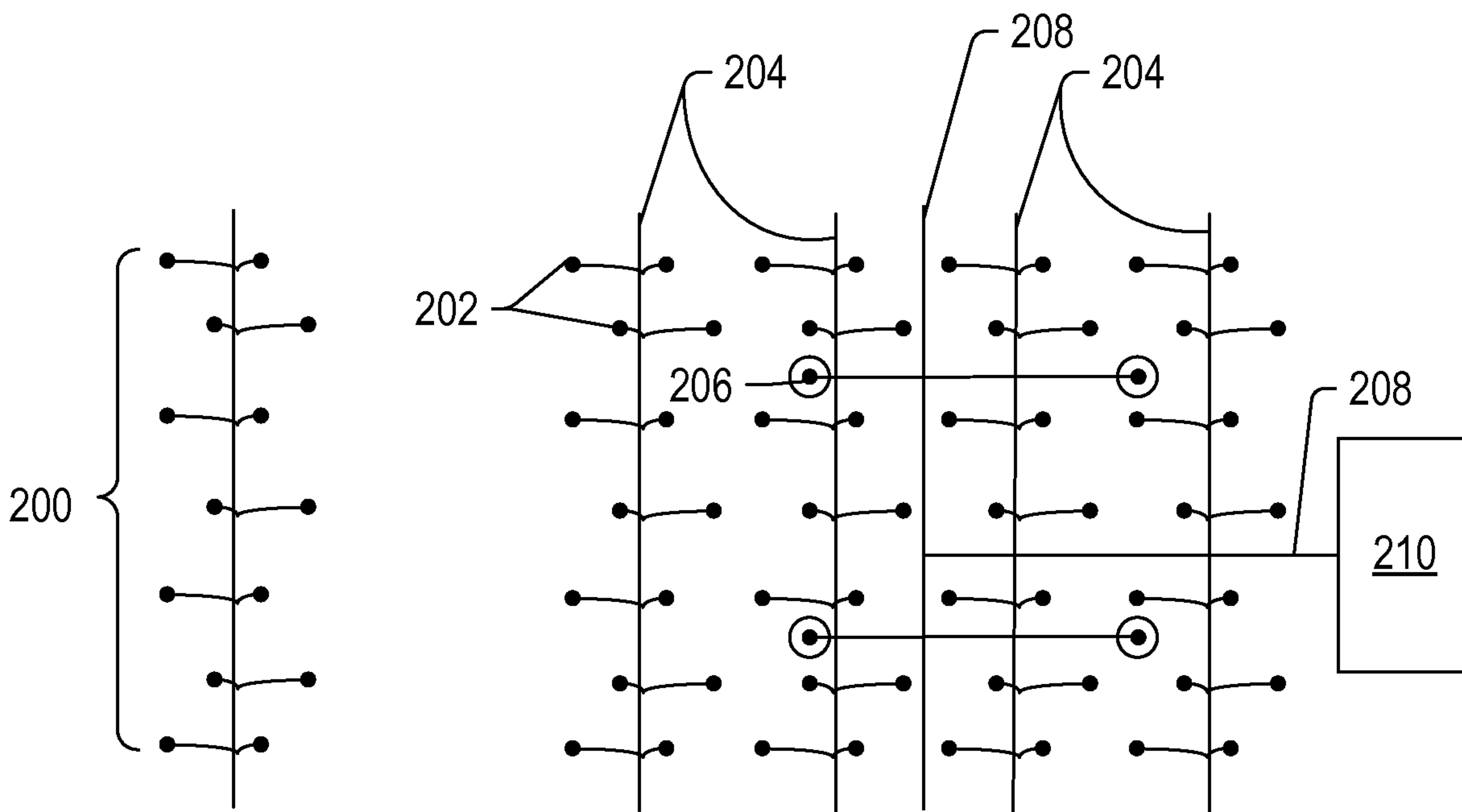
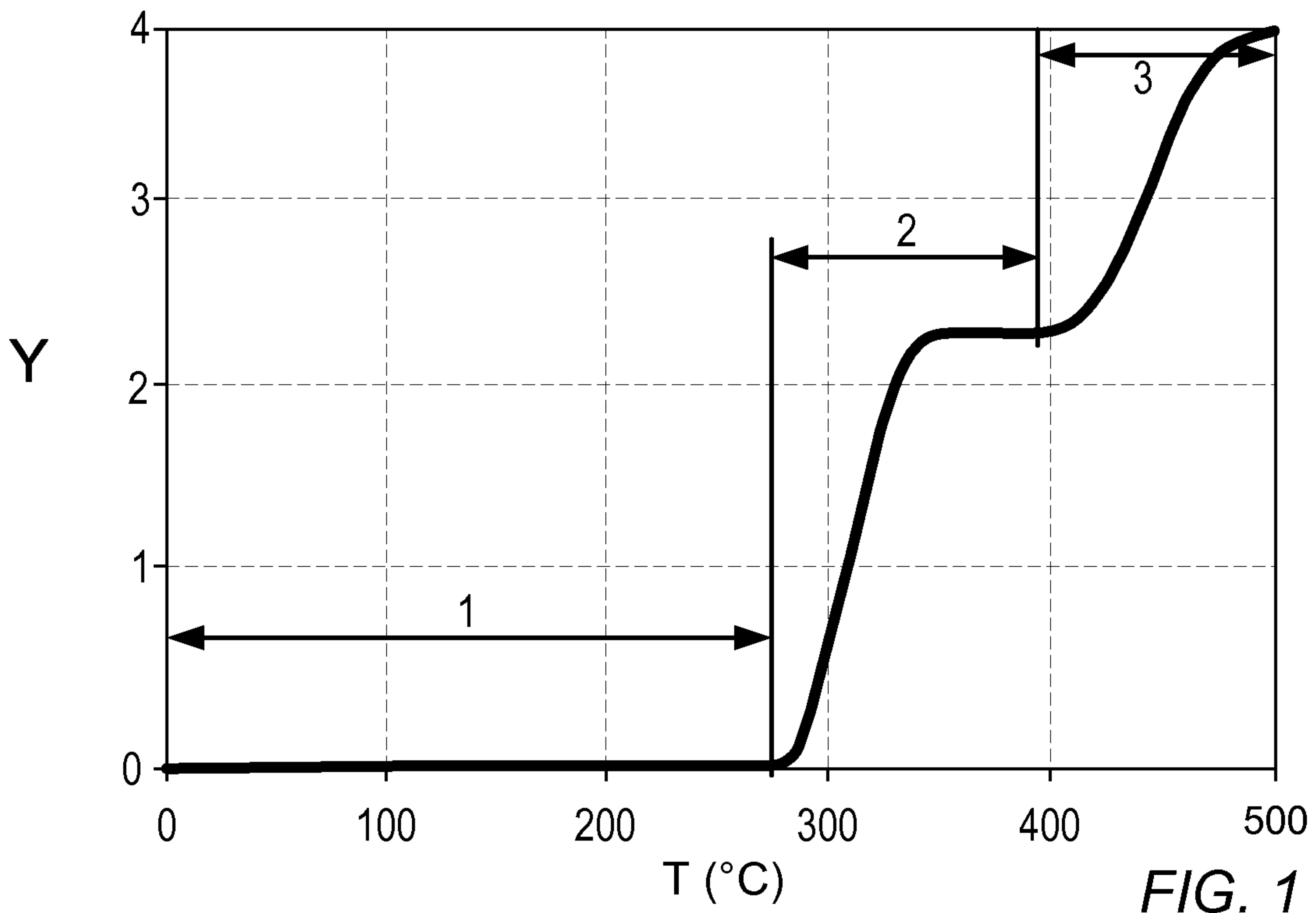


FIG. 2

