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[54] **SOLVENT/NON-SOLVENT PYROLYSIS OF SUBTERRANEAN OIL SHALE**

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[58] **Field of Search** 166/303, 272, 271, 250; 299/5

[56] **References Cited**

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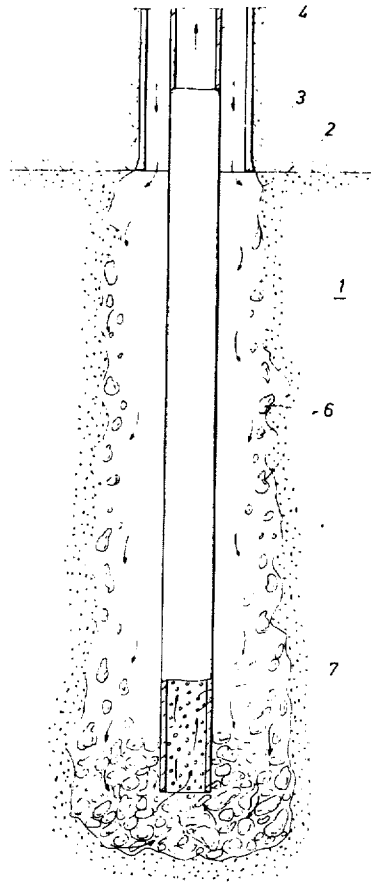
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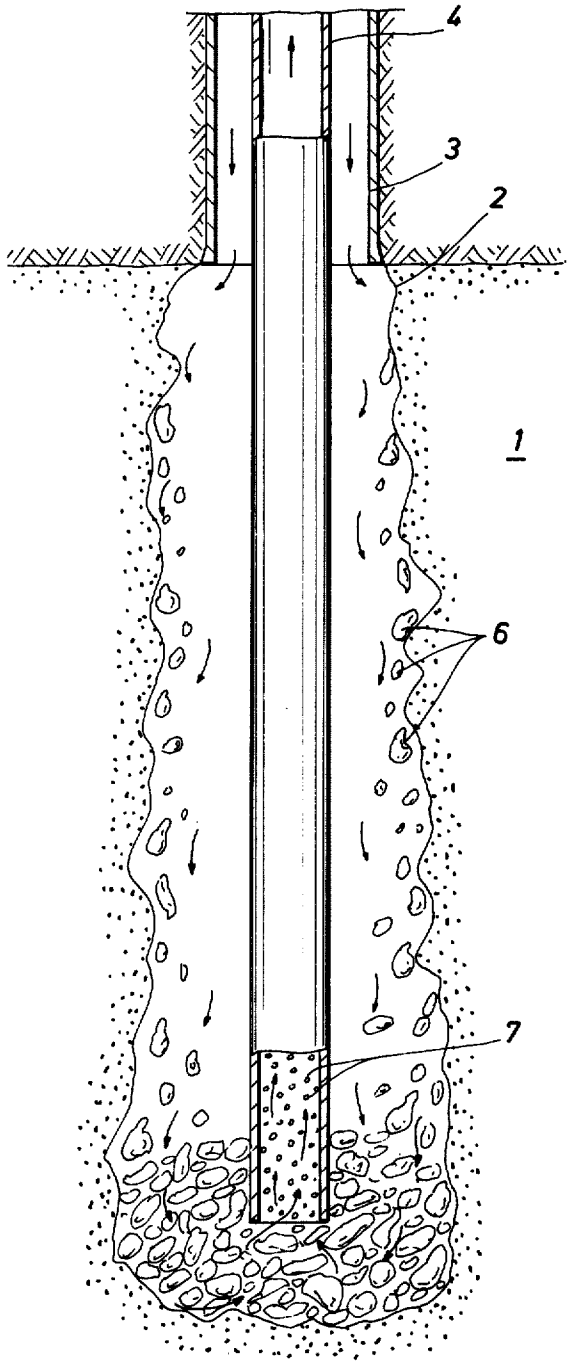
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[57] **ABSTRACT**

In a process for recovering shale oil by injecting and producing fluid into and out of a rubble-containing cavity in an otherwise substantially impermeable subterranean oil shale, the tendency for the flow path to become plugged is reduced by injecting both a hot solvent-fluid and a non-solvent-gas at rates correlated so that the cavern remains substantially free of liquid.

6 Claims, 1 Drawing Figure




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SOLVENT/NON-SOLVENT PYROLYSIS OF SUBTERRANEAN OIL SHALE

BACKGROUND OF THE INVENTION

The invention relates to producing shale oil and related mineral materials from subterranean deposits of oil shale.

Numerous subterranean oil shales are mixed with water-soluble minerals and comprise substantially impermeable, kerogen-containing, earth formations from which shale oil can be produced by a hot fluid-induced pyrolysis or thermal conversion of the organic solids to fluids. A series of patents typified by the T. N. Beard, A. M. Papadopoulos and R. C. Ueber U. S. Pat. Nos. 3,739,851; 3,741,306; 3,753,594; 3,759,328; 3,759,574 describe procedures for utilizing the water-soluble minerals in such shales to form rubble-containing caverns in which the oil shale is exposed to a circulating hot aqueous fluid that converts the kerogen to shale oil while dissolving enough mineral to expand the cavern and expose additional oil shale. In such processes, the heat transfer is aided by injecting the hot fluid into an upper portion and withdrawing fluid from a lower portion of the cavern.

However, as described in the P. J. Closmann and G. O. Suman U.S. Pat. Nos. 3,804,169 and 3,804,172, such prior cavern-utilizing processes are subject to a tendency for the flow paths to become plugged. The hot aqueous fluid flowing down along the walls of the cavern rubblizes and disaggregates portions of the shale oil into particles having sizes ranging from a few microns to several feet in diameter. The particles tend to slump or flow as a turbidity current down the walls of the cavern and pile up around the fluid withdrawal point near the bottom of the cavern. In the U.S. Pat. No. 3,804,169, a pattern of fracture-interconnected caverns and wells are arranged so that fluid injected near the top of one well is produced through a plurality of surrounding wells with the flow rates being too low to carry the solids to the production well. In the U.S. Pat. No. 3,804,172, the lower portion of such a cavern is packed with a mass of large rigid solid particles, so that the slurried solids in the slumping turbidity currents are spread over large surface areas while the fluids are flowing through the relatively large openings that exist between the particles.

SUMMARY OF THE INVENTION

The present invention relates to an improvement in a process in which shale oil is produced by forming a rubble-containing cavern within an otherwise substantially impermeable subterranean oil shale that contains water-soluble minerals, injecting fluid into the cavern, withdrawing fluid from the cavern, and recovering shale oil from fluid withdrawn from the cavern. The improvement comprises the following. A hot solvent-fluid (which is significantly miscible with at least one organic or inorganic solid or liquid pyrolysis product of the oil shale) is injected into an upper portion of the cavern. A non-solvent-gas (which has a relatively insignificant miscibility with any of said pyrolysis products) is also injected into an upper portion of the cavern. Fluid is withdrawn from the cavern from below the points of fluid injection. And, the properties and flow rates of the injected and produced fluids are correlated so that the cavern remains sufficiently liquid-free to prevent a significant plugging of the fluid flow path by the forming and screening out of fine solid particles.

DESCRIPTION OF THE DRAWING

The drawing schematically illustrates a portion of a well well within a subterranean oil formation in which the present invention is being practiced.

DESCRIPTION OF THE INVENTION

The present invention is, at least in part, premised on the following. In an oil shale recovery process in which a hot solvent-fluid (such as an aqueous fluid) is injected into and produced from a rubble-containing cavern within a subterranean oil shale that contains water-soluble minerals, the plugging of the flow path can be avoided without significantly reducing the rate of shale oil production. The kerogen in such an oil shale can be pyrolyzed while forming less fine solid particles by contacting the oil shale with a hot non-solvent-gas (such as nitrogen) that is substantially immiscible with any of the organic or inorganic solid or liquid pyrolysis products of the oil shale-rather than contacting the oil shale with a hot solvent-fluid. In treating the oil shale exposed within a rubble-containing cavern, the transferring of heat from an injected hot fluid to the oil shale along the cavern walls is significantly enhanced by injecting the fluid above the location from which fluid is withdrawn. In such a downflowing circulation, the tendency for plugging to occur in or around the fluid withdrawal location is greatly reduced when the fluid that is being circulated contains at least some non-solvent-gas. Relative to a liquid the gas is highly mobile and exerts relatively little drag effect on the movable solids. In addition, the plugging is greatly increased when undisaggregated lumps or pieces of oil shale are contacted by a hot aqueous or oil-phase liquid that tends to dissolve in and soften one or more of the organic or inorganic solid components that are exposed on the surfaces of the oil shale. The softened components deform into and around adjacent solid materials and cling to the fine particles that plug the interstices between the larger particles. The plugging is particularly severe when a stream of liquid is moving through a mass of such particles within a rubble-containing cavern in which the particles are free to move toward the point of fluid withdrawal. The relatively viscous liquid tends to entrain and carry particles until even the smallest particles are screened out in the form of a filter cake that becomes substantially impermeable.

As used herein "oil shale" refers to a substantially impermeable aggregation of inorganic solids and a predominately hydrocarbon-solvent insoluble organic solid material known as "kerogen". "Bitumen" refers to the hydrocarbon-solvent-soluble organic material that may be initially present in an oil shale or may be formed by a thermal conversion or pyrolysis of kerogen. "Shale oil" refers to the gases and/or liquid hydrocarbon materials (which may contain trace amounts of nitorgen, sulfur, oxygen, or the like, as substituents to such hydrocarbons) which can be obtained by distilling or pyrolyzing or extracting organic materials from an oil shale. "Water-soluble inorganic minerals" refer to halites or carbonates, such as the alkali metal chlorides, bicarbonates or carbonates, which compounds or minerals exhibit a significant solubility (e.g. at least about 10 grams per 100 grams of solvent) in generally neutral aqueous liquids (e.g. those having a pH of from about

5 to 8) and/or heat-sensitive compounds or minerals, such as nahcolite, dawsonite, trona, or the like, which are naturally water-soluble or are thermally converted at relatively mild temperatures (e.g. 500° to 700° F) to materials which are water-soluble. The term "water-soluble-mineral-containing subterranean oil shale" refers to an oil shale that contains or is mixed with at least one water-soluble mineral, in the form of lenses, layers, finely-divided dispersed particles, or the like.

A hot solvent-fluid suitable for use in the present process is one which is heated to a temperature of about 500° to 700° F and, at such a temperature, exhibits a significant miscibility with at least one of the organic or inorganic solid or liquid pyrolysis products of a water-soluble-mineral-containing oil shale. Such fluids preferably contain, or consist essentially of stream at a temperature and pressure causing condensation within the cavern. Such fluids may also include or comprise hydrocarbons such as benzene, toluene, shale oil hydrocarbons, oil-soluble gases such as carbon dioxide, mixtures of such fluids, or the like.

A hot non-solvent-gas suitable for use in accordance with this invention can comprise substantially any gas having a temperature of at least about 500°F and, at that temperature, having a relatively insignificant miscibility with any of the organic or inorganic solid or liquid pyrolysis products of a water-soluble-mineral-containing oil shale (e.g. having a solubility of less that about 1 part per thousand in such solid or liquid pyrolysis products). Suitable non-solvent-gases include nitrogen, natural gas, combustion gases, methane that is substantially free of higher hydrocarbons, mixtures of such gases, and the like, particularly where steam is used as the hot solvent-fluid, the hot non-solvent-gas can be injected at temperatures higher than about 700°F, for example, to enhance the rate of revaporizing the steam condensate and the drying out of the cavern.

The hot solvent and non-solvent fluids used in the present process can be injected as a mixture or as alternating slugs and can be conveyed into the cavern through the same or different conduits. The properties and flow rates of the inflowing portions of such fluids and the outflowing portions of the fluid withdrawn from the cavern are correlated so that the cavern remains liquid-free to an extent such that the outflow of fluid (with substantially all of the fluid being withdrawn from a level below the lowest level at which fluid is injected into the cavern) is not significantly impeded (by the plugging action of solids in and around the point of fluid withdrawal). As known to those skilled in the art, such correlation of properties and flow rates can be accomplished by adjusting the compositions, the injection pressures (and thus the rates), and the temperatures of the fluids being injected, adjusting the backflow resistance (and thus the flow rate) of the fluid being withdrawn from the cavern, and the like. In such an operation, a plugging-induced impeding of the outflow of the fluid in the cavern is indicated by an increase in the injection pressure that is required to sustain a given rate of injection, a decrease in the rate of inflow or outflow at a given pressure, or the like. In general, the ratio of the volume of the injected hot non-solvent-gas relative to the volume of injected hot solvent-fluid (relative to the fluid phase which that fluid will have while it is being withdrawn from the cavern) can be from about 0.5 to 1.5 and is preferably about 1.0.

As shown in the drawing, the present invention can be practiced with a relatively simple arrangement of downhole equipment. A layer of water-soluble mineral-containing oil shale **1** is penetrated by a well borehole **2**. The borehole is equipped with an outer conduit **3** and an inner conduit **4** arranged to provide a point of fluid injection, through conduit **3**, at a location above a point of fluid withdrawal, through conduit **4**. Such an oil shale can advantageously be the Green River formation in Colorado in which water-soluble minerals such as alkali metal halite and heat-sensitive carbonates such as nahcolite and trona are present in the form of beds, lenses, nodules, etc.

As known to those skilled in the art, the surface equipment should include wellhead and surface conduits, fluid storing, heating, pressurizing etc., containers and produced fluid-storing and product-separating equipment, and the like, not shown. Such equipment can be composed of conventional devices.

In a preferred procedure, a hot solvent-fluid, such as steam at a temperature and pressure of 625° F and 1852 psi, is injected, against a back pressure that maintains such as pressure at a rate of about 500–5000 B/D. The steam is preferably injected through conduit **3** to condense and flow downward along the walls of the borehole **2**, as shown by arrows, while fluid is being withdrawn at a lower depth through conduit **4**. The steam condensing along the borehole wall dissolves portions of naturally water-soluble minerals (such as the halites), thermally converts heat-sensitive carbonates (such as the nahcolites) to soluble materials that are dissolved and gases (such as carbon dioxide) that are entrained in the flowing fluid, pyrolyzes the oil shale kerogen to fluid bitumen and/or fluid shale oil materials, and disaggregates portions of the shale oil. Since some portions of the earth formation are dissolved or disaggregated faster than others (such oil shales are generally heterogeneous), rocks and lumps or pieces or rubble of oil shale and other solid materials are released to fall into the bottom of the borehole. A borehole, such as borehole **2**, is thus converted to an expanding, rubble-containing, cavern within the oil shale. Alternatively, a rubble-containing cavern or cavity can be formed by an initial solution mining of water-soluble minerals (such as trona, or the like), with or without hydraulic and/or explosive fracturing (to extend the zone of permeability and/or facilitate the enlargement of such a cavern). Such a cavern can comprise substantially any opening and/or network of fractures in which pieces or rubble of oil shale are present and are free to be contacted and moved by a circulating fluid.

In accordance with the present invention, a hot non-solvent-gas (such as nitrogen) is injected along with the steam (continuously or in the form of alternating slugs) at a rate such that the flow of fluid into the bottom of conduit **4** remains substantially unimpeded by the forming and screening out of fine solid particles. Where the injection is continuous, the fluid being withdrawn will be a predominately gaseous fluid containing suspended droplets or particles **7** of liquid and/or fine solids. Where alternate slugs are injected, some liquid may accumulate in the bottom of the cavern (e.g. during the injecting of the hot solvent fluid) and, while the non-solvent-gas is being injected, the fluid being withdrawn may be either a liquid containing dispersed droplets or particles **7** of gas and solids or a gas-

containing dispersed droplets or particles 7 of liquid and solid. The liquid is removed soon enough to keep the cavern, on the average, sufficiently liquid free so as to prevent the liquid-induced increase in disaggregation, particle-softening and particle-entraining from forming a filter-cake that is tight enough to significantly plug the flow path.

Where the injected hot solvent-fluid is steam, the heating of the hot non-solvent-gas can be advantageously effected by direct or indirect heat exchange with the steam being generated and/or injected. In such an operation the steam can be superheated so that some steam remains uncondensed (and thus acts similar to a hot non-solvent-gas) during its residence within the cavity. But, the proportion of a hot non-solvent-gas that is non-condensible (such as nitrogen) should be at least about 50 percent by volume of the injected steam. This ensures a substantially continuous removal of at least a significant portion of liquid.

Where alternate slugs of hot solvent and non-solvent fluid are injected, a selected rate of flow can be maintained during the injection of each slug. During the hot solvent-fluid injection, a need for a conversion to a hot non-solvent-gas injection can be identified by a rise in injection pressure required to maintain the selected rate of flow. The surface equipment for injecting such fluids is preferably arranged so that, in case of a relatively severe flow impairment, the direction of flow can be temporarily reversed (so that it becomes opposite that indicated by the arrows) to disrupt any pore-blocking or bridging patterns of accumulated fines and larger particles.

What is claimed is:

1. In a shale oil-producing process in which a rubble-containing cavern is formed within an otherwise substantially impermeable subterranean oil shale that contains water-soluble minerals and fluid is injected into and withdrawn from the cavern, the improvement which comprises:

in an upper portion of said cavern, injecting hot solvent-fluid having a significant miscibility with at least one organic or inorganic solid or liquid pyrolysis product of said oil shale;

in an upper portion of said cavern, injecting hot non-solvent-gas having a relatively insignificant miscibility with any of the organic or inorganic solid or liquid pyrolysis products of said oil shale;

withdrawing fluid from said cavern from a level below any at which fluid is injected into the cavern;

correlating the properties and flow rates of the inflowing and outflowing portions of said fluids so that the cavern remains sufficiently liquid-free to prevent a significant plugging of the fluid flow path; and

recovering shale oil from fluid withdrawn from said cavern.

2. The process of claim **1** in which said hot solvent-fluid and hot non-solvent-gas are injected in the form of alternating slugs of the respective fluids.

3. The process of claim **1** in which said hot solvent-fluid and hot non-solvent-gas are injected in the form of a mixture of said fluids.

4. The process of claim **1** in which said hot solvent-fluid is steam.

5. The process of claim **1** in which said hot non-solvent-gas is nitrogen.

6. The process of claim **1** in which said hot non-solvent-gas is combustion gas.

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