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United States Patent

Wise

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[54] **EQUILIBRATED SOIL-GAS SAMPLING**

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[51] **Int. Cl.**.....**G01n 1/00,** G01n 31/00
[58] **Field of Search**...73/19, 23, 155, 152, 61, 421.5; 23/230 EP, 232

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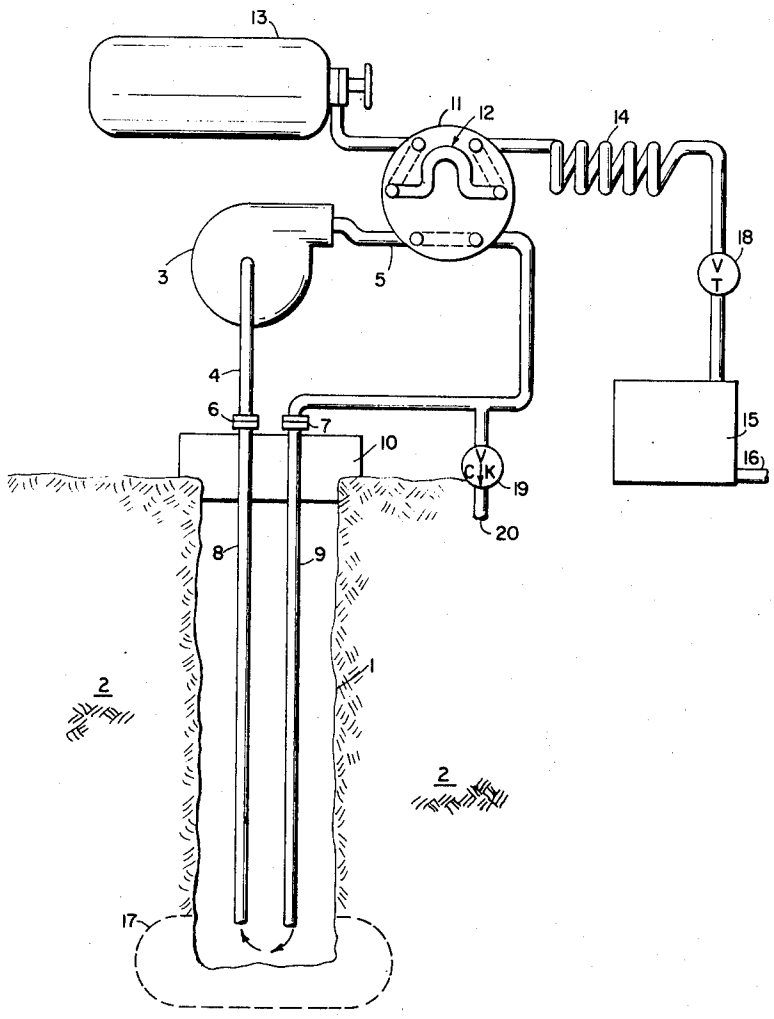
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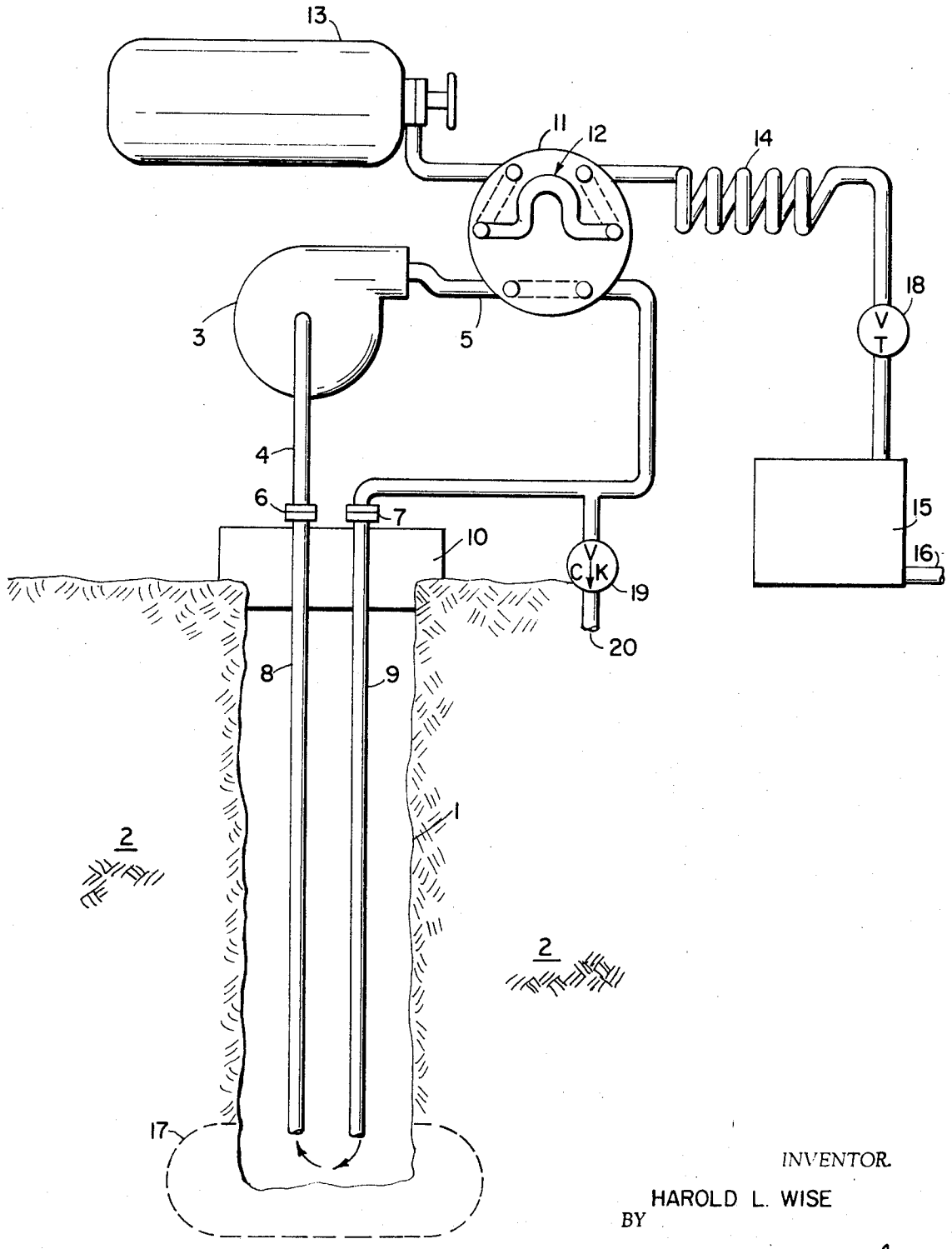
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[57] **ABSTRACT**

The sampling of the concentration of a selected fluid in a subterranean earth formation is improved by circulating a fluid into repetitive contacts with the earth formation and measuring the concentration of the selected fluid in the circulating fluid when the concentration is at a level at which its rate of change is low relative to that exhibited in the initial stage of the fluid circulation.

10 Claims, 1 Drawing Figure





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EQUILIBRATED SOIL-GAS SAMPLING

BACKGROUND OF THE INVENTION

The invention relates to the sampling of soils or other subsurface earth formations. Such a sampling is often used to provide maps or surveys of the concentration with location of at least one selected fluid. Such maps are indicative of compositions and/or events within the sampled or underlying subterranean earth formations.

Numerous methods and devices have been proposed for sampling the concentration of a fluid, such as a hydrocarbon, in a subterranean earth formation. Such operations are made difficult by the tendency for the concentrations of such fluids to be very small; generally less than one part per million. At such relatively low concentrations the previously employed sampling procedures have tended to provide inconclusive results. The concentrations that were measured at times and locations at which the measured values should have been substantially equal have tended to fluctuate by amounts that were large relative to the amounts that were present, have tended to follow changes in the concentrations in the ambient atmosphere, have tended to vary widely from one sample to the next, etc.

Fluids such as hydrocarbons tend to escape from subterranean locations and migrate up through the overlying earth formations. Some of the migrating fluids become adsorbed on the solid components of the earth formations and some become dissolved or entrained in the fluid components. The hydrocarbons associated with both the solid and liquid components of an earth formation can be measured by obtaining and analyzing a core sample; but, it is relatively expensive to collect and analyze such samples. In general, the previously proposed procedures for sampling subsurface earth formations are based on analyses of the fluid encountered by a borehole that is opened into the earth formation. In such procedures, the pressure within the borehole is reduced to one which is less than that within the earth formation, a portion of inflowing fluid is collected, and measurements are made of the hydrocarbon content of that fluid. At depths above the water table the so-collected fluids are usually gaseous and at depths greater than the water table they are usually liquid.

A primary object of the present invention is the provision of an economically feasible sampling procedure that is responsive to any natural correlation that may exist between the amounts and types of a selected fluid, such as a hydrocarbon, that are contained in subsurface earth formations that have different horizontal or vertical locations.

In a permeable earth formation the mineral solids are adapted to adsorb varying amounts of hydrocarbons of different compositions or types. The solid components are surrounded by one or more fluids that each have a different degree of miscibility with hydrocarbons of varying types. If the naturally occurring (or connate) fluid in the earth formation is sampled, its hydrocarbon content is a function of the chemical composition and phase of the fluid as well as the type and amount of hydrocarbons that may have migrated into or through that portion of earth formation. If the fluid contents are all that is analyzed, this is apt to provide results that are misleading with respect to the hydrocarbon contents of

differently located portions of earth formations. For example, if portions of the same type of permeable earth formation solid materials are located above and below the water table and are traversed by the same upward migration volatile hydrocarbons, the hydrocarbon content of the fluids in the upper location (e.g., gases similar to the ambient atmospheric gas) would be distinctly different from those of the fluid in the lower location (e.g., an aqueous solution of one or more salts). In other words, generally similar amounts and types of hydrocarbons may be adsorbed on the earth formation solids in both locations, but distinctly different amounts and types may be dissolved and/or entrained in, for example, a fully miscible gaseous fluid and a substantially immiscible aqueous liquid.

SUMMARY OF THIS INVENTION

This invention provides an improved process for measuring the amount of a selected fluid that is present in a subsurface earth formation into which a borehole is opened. In the present process a fluid that contains a known and relatively small amount of the fluid being sampled is circulated into repetitive contacts with the earth formation and the concentration in the circulation fluid of the fluid being sampled is measured at a substantially equilibrium value at which its rate of change is low relative to that exhibited in early stages of the fluid circulation.

The present invention is particularly useful for measuring the concentration with position of one or more selected fluids that may be indicative of a subterranean deposit or source of such a fluid. It is also useful for monitoring a concentration of a selected fluid with time (or other parameter) in order to detect a presence or an event in the earth formation being sampled or in an underlying earth formation.

DESCRIPTION OF THE DRAWING

The FIGURE is a schematic illustration of equipment disposed for sampling an earth formation in accordance with this invention.

DESCRIPTION OF THE INVENTION

In the system shown in the drawing, a borehole **1** is opened into a subsurface earth formation **2** to be sampled with respect to its content of a selected fluid such as ethane. Pump **3** is arranged to circulate fluid through pump inflow and outlet conduits **4** and **5** which are attached, by means of connectors **6** and **7**, to borehole conduits **8** and **9**. The borehole conduits extend through and are supported by borehole closure plug **10**. The connectors **6** and **7** are arranged so that conduits **4** and **5** can be disconnected from the borehole conduits and connected together, by means of detachable conduit (not shown) in order to confine the pump-driven fluid circulation path to a surface location. Multiple port valve **11** is arranged to switch a sample trap loop **12** into and out of the pump-driven fluid circulation path.

Valve **11**, in the position shown, connects a source of pressurized fluid **13** so that fluid flowing from source **13** displaces fluid from the trap loop **12** into chromatographic column **14**, and then into a measuring device **15**, and, subsequently, out through an exhaust port, **16**.

Flow-controling valve means, such as throttle valve **18** and check valve **19**, can advantageously be used when operating the column **14** at a pressure higher than that generated by pump **3**. Throttle valve **18** can restrict the rate at which fluid flows from a relatively high pressure at source **13** to atmospheric pressure at exhaust port **16**, thus maintaining a selected relatively high pressure within column **14**. It also causes trap loop **12** to become filled with gas at about the pressure in column **14**. Where the pressure in column **14** is greater than that provided by pump **3** the amount of gas in loop **12** is more than that in the same-sized portion of conduit **5**. Repeated switchings of trap loop **12** between the higher and lower pressures tends to dilute the fluid being recirculated within the borehole by removing relatively small amounts and replacing them with larger amounts. Such a dilution is preferably avoided by arranging check valve **19** to allow an outflow through port **20** in response to a pressure above that provided by pump **3**.

In a preferred mode of operating the system shown in the drawing, the surface located portion of the circulation path is purged and filled with a substantially hydrocarbon-free gas, such as a "clean" air. Such an operation preferably includes an interconnection of the pump inflow and outflow conduits **4** and **5** through connectors **6** and **7** and a detachable conduit (not shown) to form a limited circulation pat that is closed, except for the exhaust through check valve **19**. This limited circulation path is preferably purged and filled with hydrocarbon-free fluid from a source such as source **13**. When the borehole is drilled, plug **10** is inserted promptly to isolate the borehole form atmospheric gases. The portions of the connectors **6** and **7** that are attached to the borehole conduits **8** and **9** are preferably arranged so that they close the ends of those conduits when the conduits are disconnected from the surface located portion of the circulation path.

In operating the invention, the circulation of a hydrocarbon-free gas into repetitive contacts with the earth formation is initiated with the system arranged as shown in the drawing, except that valve **11** is positioned so that trap loop **12** is in the path of the pump-drive circulation into the borehole. During this operation, the fluid within the borehole above the lower ends of the conduits **8** and **9** remains substantially static. The fluid which circulates within the borehole tends to follow the arrows and to selectively contact the portions of earth formation to that are exposed within the region bounded by the broken line **17**.

In a shallow borehole, e.g., one having a depth in the order of 5 feet, the fluid pressure within the earth formation is substantially atmospheric pressure. By selecting conduits **4**, **5**, **8** and **9** to have substantially equal sizes and effective flow resistances, the pressure of the fluid being circulated within the borehole can be maintained at substantially atmospheric pressure. This causes the exposed earth formations in zone **17** to be repetitively contacted while little or no fluid is being lost into or withdrawn from the portions that are not swept by the fluid circulating within the borehole.

In general, the boreholes used in the present invention can be relatively deep or shallow and can be freshly drilled or pre-existing. Freshly drilled shallow boreholes are preferred. Particularly suitable boreholes are drilled with an augering type of device which requires no circulation of drilling fluid. The augering of a borehole tends to mechanically displace earth formation solids so that a limited amount of fluid is drawn into the lower part of the borehole. The amount drawn in is only that required to replace the material that is removed and it is drawn in from the earth formations adjacent to the lower part of the borehole. The freshly drilled boreholes are preferably promptly plugged or packed-off at least at a depth near the depth at which the sampling is to be conducted. Field tests have demonstrated that even where the atmosphere is polluted with significant and varying amounts of hydrocarbons, consistent and reproducible measurements of hydrocarbon concentrations can be made by: removing solid material from subsurface earth formations to form a borehole while inflowing fluid substantially only from surrounding subsurface earth formations, promptly isolating the portion of the borehole wall which is to be sampled from fluids in the overlying atmosphere, and sampling the hydrocarbon concentration of the so-exposed earth formation by circulating a substantially hydrocarbon-free fluid and measuring its hydrocarbon content as described above.

In relatively deep boreholes, the exposed earth formations may contain a liquid having a significantly high pressure and temperature. In such situations the sample-entraining fluid, i.e., the fluid containing a known and relatively insignificant amount of the fluid whose concentration is being sampled, can be either a gas or a liquid. In either situation the borehole is preferably equipped with conduits, packers, etc., arranged to confine the fluid being circulated so that it makes repetitive contacts with the earth formations that are exposed along a selected depth interval. Such a circulating fluid is preferably circulated against a back pressure adjusted to provide a downhole pressure substantially equalling the pressure of the fluid within the exposed earth formations. The measurements of the concentration of the selected fluid within the circulating fluid are preferably accompanied by measurements of the pressure and temperature of the circulating fluid.

The fluid that is sampled or surveyed by the present invention can be substantially any gas or liquid. One or more hydrocarbons containing from about one to 10 carbon atoms, carbon dioxide, nitrogen, oxygen, hydrogen sulfide, or the like comprise preferred fluids to be sampled.

The sample-entraining fluid which is circulated into repetitive contacts with the earth formation being sampled can be substantially any pumpable fluid the (a) is at least substantially miscible with the fluid being sampled and (b) is substantially free of the fluid sampled. In general, for sampling the concentration of either an organic or inorganic gas, vapor, air or liquid, that is substantially free of the fluid being sampled is a preferred sample-entraining fluid. In certain locations, the ambient atmospheric air substantially free of contaminants. Such uncontaminated air can be tanked and utilized in the manner illustrated in the drawing and/or can be pressurized by means of the compressor or blower to displace it into the circulating and analyzing system.

The rate and duration of the circulation of sample-entraining fluid can vary over a relative wide range. In a

given situation, the sample-entraining fluid should be circulated until the rate of change of the concentration of the fluid being sampled is low relative to its rate of change in the early stages of the fluid circulation. This amounts to sampling a substantially equilibrium concentration. It is the preferred concentration to be measured in accordance with the present invention as that which is representative of the sampled portion of an earth formation. It is a concentration at which the rate at which the selected fluid is being desorbed (or otherwise released from or discharged from the exposed portion of the earth formation) is substantially equal to (or is substantially constant with respect to) the rate at which that fluid is adsorbed on the exposed earth formation. In a given situation the attainment of this substantial equilibrium concentration can be determined by repetitively measuring the concentration during the fluid circulation and noting the circulation time required for the attainment of a relatively low rate of change of concentration. Where the same type of formations are being sampled with the same sample-entraining fluid and the same size of boreholes, circulation equipment, circulation rate, and the like, are used, the making of repetitive measurements can be omitted and a substantially equilibrium concentration can be measured by making each of the measurements at about the same times after the initiations of the circulations.

While the present invention is not limited to any particular mechanism or theory of operation, it appears to selectively sample fluid which is either being desorbed by the contacting of the earth formation with the circulating sample-entraining fluid or is flowing through the contacted portion of the earth formation while it is being contacted by the sample-entraining fluid. After the borehole has been opened, the fluid which was present in the surrounding portions of the earth formation prior to the drilling of the borehole is, in effect, held back and kept out of the path of the circulating sample-entraining fluid. Since the sample-entraining fluid is circulated at a pressure equalling the formation fluid pressure, its flow tends to be confined to a region near the inflow and discharge openings of the conduits to which it is circulated. The present invention thus minimizes variations in the measured concentrations that might be due to variations in the type of fluid that was initially present in different portions of the earth formation.

The consistency of the attainment of substantially equilibrium concentrations and the reproducibility of the present sampling procedure have been demonstrated in repetitive measurements in earth formations in which the concentrations of the hydrocarbons should be the same. The boreholes were drilled to a depth of about 5 feet with a bronze auger having a diameter of about 4 inches. The measurements were made with sampling equipment of the type shown in the drawing. The sample-entraining fluid was atmospheric air that was preprocessed to render it substantially free of hydrocarbons. In a region and a time in which the concentrations of the measured hydrocarbon in the ambient atmosphere ranged from 80 to 100 units, measurements in a series of boreholes in equivalent locations settled to relatively slow and constant rates of change within 1 to 2 minutes after the starts of the circulation of the sample-entraining fluid. Within a period of 30 minutes the measured concentrations remained consistently with a range of from 1,400 to 1,500 units in boreholes of relatively high hydrocarbon concentration and within a range of from 10 to 20 units in boreholes of relatively low hydrocarbon concentration. Note that neither range seems likely to have involved significant contamination by the ambient atmosphere, in which the hydrocarbon concentration was distinctly different.

Such measurements have confirmed the conclusion that (1) consistent and representative substantially equilibrium concentrations can be measured at equal times after the starts of the circulations of the sample-entraining fluid (2) atmospheric contamination can be avoided (3) the measurements are reproducible in the range of less than one part per million concentration (4) in boreholes in which the amounts of hydrocarbons are high, within such a range, the concentrations tend to be relatively slowly increasing with time and (5) in boreholes in which the concentrations are low within such a range the concentrations tend to be relatively slowly decreasing with time. The location of boreholes in which the concentration of hydrocarbons increased with time seem to be in the direct paths of fluids that are migrating through the earth formations being sampled. Such an increase is also observable in the concentrations of other gases such as CO_2, N_2, etc., that may be copresent with hydrocarbons in gas reservoirs.

What is claimed is:

1. A geochemical exploration process, which comprises:
   - opening a borehole into a subsurface earth formation;
   - installing within said borehole means for conveying fluid to and from selected depths within the borehole;
   - installing a packing or plugging means adjacent to the section of borehole that contains said selected depths to isolate that section by preventing the flow of fluid between the wall of the borehole and the exterior of said means for conveying fluid;
   - circulating a fluid that contains a known and relatively insignificant concentration of a selected fluid into repetitive contacts with earth formations exposed along the wall of the borehole at said selected depths; and
   - measuring the concentration of the selected fluid within the circulating fluid when the rate of change of its concentration is slow relative to the rate of change in an initial stage of the fluid concentration.

2. The process of claim 1 in which the pressure of the fluid circulating within said borehole is kept substantially equal to the pressure of the fluid in said exposed earth formations.

3. In a process for measuring the concentration of at least one hydrocarbon in a subsurface earth formation that is exposed along the wall of a borehole, the improvement which comprises:
   - mechanically isolating a selected depth within said borehole;
   - circulating fluid having a known and relatively insignificant concentration of the selected hydrocarbon into repetitive contacts with the earth formation

that is exposed at said selected depth within the borehole; and

measuring the concentration of the selected hydrocarbon in the circulating fluid when the rate of change of its concentration is slow relative to that exhibited near the start of said fluid circulation.

4. The process of claim **3** in which the pressure of the circulating fluid is kept substantially equal to the pressure of the fluid within the subsurface earth formation.

5. The process of claim **3** in which the measurements are made in a plurality of boreholes by circulating the same type of fluid into each borehole.

6. The process of claim **3** in which the measurements are made of at least one inorganic component that is copresent with at least one hydrocarbon.

7. The process of claim **3** in which the borehole is formed by mechanically removing solids while inflowing fluid from the adjacent subsurface earth formations without pumping any significant amount of fluid into the borehole from a surface location.

8. The process of claim **7** in which the borehole is formed by an augering out said solids to create a reduced pressure near the bottom of the borehole.

9. The process of claim **3** in which the circulation of fluid is started substantially immediately after the borehole is opened into the earth formation.

10. The process of claim **3** in which the circulated fluid is air that contains less than one part per million of any hydrocarbon.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,685,345 Dated August 22, 1972

Inventor(s) Harold L. Wise

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

The patent is assigned to Shell Oil Company, New York, New York, a Corporation of Delaware.

Signed and sealed this 23rd day of January 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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TEB:GP

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,685,345 **Dated** August 22, 1972

Inventor(s) Harold L. Wise

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

The patent is assigned to Shell Oil Company,

New York, New York, a Corporation of Delaware.

Signed and sealed this 15th day of May 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents