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(54) **USE OF DEUTERIUM OXIDE-DEPLETED WATER AS A TRACER IN DOWNHOLE AND CORE ANALYSIS APPLICATIONS**

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(57) **ABSTRACT**

A method of ascertaining or measuring subterranean events includes use of deuterium oxide-depleted water as a tracer. The presence of deuterium oxide-depleted water may be measured at a subterranean location by means such as core sampling, for any purpose for which tracers are known to be useful. For example, the presence or absence, and level, of deuterium oxide-depleted water in a core sample may be used to determine fluids saturation levels, porosity and permeability, as well as other subterranean formation and/or reservoir characteristics important to the oil and gas production industry.

USE OF DEUTERIUM OXIDE-DEPLETED WATER AS A TRACER IN DOWNHOLE AND CORE ANALYSIS APPLICATIONS

BACKGROUND

[0001] 1. Field of the Invention

[0002] This invention relates to the field of tracers used in a variety of applications, and in particular to methods of ascertaining or measuring subterranean events wherein tracer migration may occur.

[0003] 2. Background Art

[0004] The use of so-called "tracers" in a variety of applications is well known. "Tracers" represent a variety of chemical compounds that, under the conditions of use, act or react in a predictable way such that their presence, absence or activity in a particular location may be detected. This detection is useful in ascertaining and/or measuring events occurring at that location, i.e., in obtaining information about a particular microcosm such as, for example, a particular downhole or formation region of a drilling site.

[0005] Tracers that have traditionally been used in oil and gas drilling applications include, for example, salts of various types, such as potassium chloride, in solution; inert gases, such as krypton or xenon; and various hydrocarbon compounds. These materials operate to "tag", i.e., act as a tracer in, oil, gas, steam or water which is introduced into the subterranean formation or well-bore using any of a wide variety of known equipment and/or methods. Other materials that may be used as tracers are so-called "heavy water", which is deuterium oxide, and tritium. Both deuterium oxide and tritium are effective for tagging purposes, but each suffers from some drawback. For example, deuterium oxide is relatively expensive because of the ratio of water required to form the desired product (about 10 tons water to prepare 1 kg deuterium oxide). Furthermore, while deuterium oxide can be purchased in relatively pure form, it is subject to very strict import and/or export restrictions. In contrast, tritium is somewhat less expensive and less restricted than deuterium oxide. However, tritium is still more expensive than many other tracers and may be undesirable or less desirable for certain applications.

[0006] Thus, what is needed in the art is a tracer material which is effective in applications where it will be employed, and which represents an economically feasible and acceptably safe material.

SUMMARY

[0007] An object of the invention is to provide a tracer material which may be effectively used in subterranean applications.

[0008] Another object of the invention is to provide a tracer material which may be used in subterranean or surface applications within parameters of acceptable expense and safety.

[0009] In carrying out these and other objects of the invention, there is provided, in one aspect, a method of ascertaining or measuring an event comprising using deuterium oxide-depleted water as a tracer.

[0010] In another aspect, there is provided a method of ascertaining or measuring a subterranean event comprising transporting deuterium oxide-depleted water, as a tracer, to a first subterranean location. The tracer is given a time period sufficient for it to migrate to a second subterranean location, if such migration is possible. A tracer detection means or method is then employed to detect the tracer in the second subterranean location.

[0011] In still another aspect, there is provided a method of ascertaining or measuring filtrate contamination of a subterranean formation. This method comprises transporting deuterium oxide-depleted water, as a tracer, to a downhole location. This downhole location has, adjacent to it, a subterranean formation wherein fluid is located. A time is allowed, sufficient for the tracer to infiltrate the adjacent subterranean formation, assuming such infiltration is possible. A sample of the subterranean formation is then obtained, such that the fluid therein is preserved. Finally, the amount of tracer in the fluid is measured.

DETAILED DESCRIPTION

[0012] The invention's method involves use of deuterium oxide-depleted water as a tracer. Deuterium oxide is itself the entity that has been colloquially termed "heavy water". It is, in its relatively pure form, a compound formed of three atoms, in which one of the two hydrogen atoms contains one extra neutron, i.e., it is HD0 rather than $H_2\mathbf{0}$. Deuterium thus can be distinguished from hydrogen by virtue of its higher atomic mass. Deuterium oxide is naturally occurring, and is virtually always present in natural waterways, including both surface and subterranean waters, in amounts frequently ranging from about 100 to about 200 ppm, generally from about 120 to about 180 ppm, and most frequently from about 130 to about 160 ppm.

[0013] Various methods have been developed to prepare so-called heavy water. For example, distillation, condensation and electrolysis means may be employed for this purpose, resulting in concentration of deuterium oxide in ordinary water. A by-product of some of these methods is deuterium oxide-depleted water. For convenience hereinafter, this deuterium oxide-depleted material will be referred to as "light water", in contrast with deuterium oxide-rich "heavy water". Light water is commercially available having deuterium present in amounts of only about 1 to about 3 ppm, but for purposes herein and in some non-limiting embodiments, the term "light water" will be used to refer to water in which deuterium levels are anywhere from about 0 ppm to about 50 ppm, and in other non-limiting embodiments from about 0 ppm to about 25 ppm.

[0014] The advantage of using light water in tracer applications, particularly for downhole purposes, is that the light water may be distinguished from other water, such as water typically present in formations or from municipal water sources, by the light water's relatively reduced levels of deuterium or deuterium oxide. While light water is generally more expensive than such formation or municipial water, its cost is generally acceptable for oil industry tracer purposes and it is generally considered to be relatively safe. It is therefore also generally free of export, import or usage restrictions in most, if not all, jurisdictions.

[0015] Since deuterium and/or deuterium oxide can be both detected and quantified using a variety of methods, measurements thereof, taken in or from samples obtained from a subterranean formation may be used to determine whether the formation has been infiltrated by the deuterium oxide-depleted water. The deuterium or deuterium oxide may be detected by, for example, methods such as conventional mass spectrophotometry, gas chromatograph-mass spectrophotometry, HPLC mass spectrophotometry, and nuclear magnetic resonance (NMR) imaging, including but not limited to both downhole and surface use thereof. Those skilled in the art will be aware of procedures for appropriate sample obtention and testing of such samples for analysis by any or all of the above means.

[0016] In the method of the invention a tracer detection means or method is employed. In the case of a tracer detection means, which may be selected to be specific to the means that will be employed for analysis, it may be generally described as any apparatus that initiates a detection signal upon locating an amount of deuterium or deuterium oxide. This signal predictably varies in some way, according to the amount of deuterium or deuterium oxide located. This signal is then transferred to an associated detection signal receiving and interpreting means (which may be a single means or two or more separate means), which provides the information to the user in an appropriate form. Such form may be, in non-limiting embodiments, a read-out means, such as a meter or graphic means, and/or another type of means, such as a means for directly or indirectly modifying events relating to the location of the original detection signal or another location, such as the location from which a specific coring sample was obtained. In the case of a tracer detection method, it may generally be described as any procedure, or series of procedures or protocols, that may serve to detect and, in some cases, to quantify the tracer. These may include a variety of combinations of sampling, preservation, extraction, isolation, analysis, and/or identifying operations. In many embodiments both a tracer detection means and a tracer detection method may be effectively used.

[0017] Such tracer detection means or method may be employed in various applications such as conventional drilling core analysis, in which extracted core samples are evaluated. Such evaluation may be carried out to determine various properties of the formation and/or reservoir, such as porosity, permeability, fluid saturation, and so forth. The invention may also be employed in cases of, in one embodiment, sponge coring, in which a cylindrical core is cut from a subterranean formation and transported to the surface for analysis. In this case, an absorbent, i.e., sponge-like, material, hereinafter termed the "sponge", is used to line the core barrel assembly and absorb any fluid to which it is exposed. This is particularly useful where the ambient atmospheric pressure to which the core sample is exposed upon extraction to the surface is significantly less than the downhole pressure. The difference in pressure causes the formation's gases within the core sample to expand and be expelled from the core as it rises to the surface, while the generally annular sponge absorbs and preserves the contacted fluid for later analysis. The fluid extracted may be formation fluid, drilling mud fluid, or a combination thereof, depending on factors inherent in the fluid's location in the core sample, the properties of the formation, and the obtention and processing of the core sample.

[0018] In such embodiment the light water tracer may be introduced into the formation, using any known method and/or equipment, at a predetermined point. Such is most conveniently downhole, in conjunction with or incorporated into a drilling mud, but alternative locations may also be selected. The core sample is then taken, in some non-limiting embodiments from a portion of the subterranean formation that is adjacent to a well-bore. The presence, or absence, of the tracer therein, and its quantification may then be determined by means of analyzing the fluid that is extracted from the sponge. Part of this analysis may, in this embodiment, include use of a retort distillation unit or Dean and Stark apparatus for removal of the water from the sponge, followed by hydrolysis thereof. Using appropriate time calculations, as well as the measurement of the amount of light water tracer introduced, it is then possible to determine formation parameters such as porosity, permeability and fluids saturation. Other information obtainable through use of this tracer include, but are not limited to, for example, identification of oil zones for secondary and tertiary recovery, oil/water contact zones, and transition zones.

[0019] It will be generally understood by those skilled in the art that if the level of deuterium or deuterium oxide at a specific location in the sponge (or in a specific discrete sponge liner) is found to be less than would be expected of formation or drilling mud-associated water alone, such as, in one embodiment, less than about 50 ppm, it will then be inferable that the introduced deuterium oxide-depleted water has entered the corresponding area of the core at that location. In other words, the formation will have been infiltrated or contaminated by the "filtrate", which is whatever material carries the light water, e.g., a drilling mud, in combination with the light water tracer itself. If the amount of deuterium is found to be very low, such as, in another embodiment, less than about 25 ppm, it will be inferable that an even greater proportion of the injected light water has reached the core. Thus, filtrate contamination of the formation will have been confirmed.

[0020] Deuterium oxide-depleted water may also be used as a tracer in other types of coring, such as, in non-limiting embodiments, conventional, high torque, low invasion, high temperature/high pressure, horizontal, deepwater, gel, oriented, slimhole, and the like. It may also be useful in a wide variety of other drillsite applications, such as, in non-limiting embodiments, fracturing, acidizing, cementing, fluid loss, depth control, field flood, and the like. It may additionally be useful in association with equipment such as the Modular Formation Dynamics Tester (MDT) (produced by Schlumberger), which tests and samples a variety of formation types to determine reservoir pressures, permeability, temperature, and the like, as well as with other types of Repeat Formation Testing (RFT) methods. Those skilled in the art will be aware of the wide application of tracers in general and will understand the benefits and advantages of substituting light water for certain tracers conventionally used in these and related applications. Nothing herein shall be construed as prohibiting simultaneous or sequential use of one or more additional tracers, such as, for example, tritium, for related or unrelated purposes.

[0021] The invention having been generally described hereinabove, those skilled in the art will appreciate that various modifications may be made within the scope of the invention, as defined by the claims appended hereto. Many potential embodiments may be envisioned by those skilled in the art, including, for example, application to a wide variety of drillsite uses, involving a wide variety of types of equipment and methods of detection, quantification, analysis, transmission/receipt, interpretation, and the like, as well as uses of light water tracer having deuterium levels other than those explicitly disclosed herein.

[0022] The following examples are provided merely to further illustrate the invention for the purpose of increasing the reader's overall understanding of it. As such they represent additional, but non-limiting, potential embodiments of the invention.

EXAMPLE 1

Hypothetical

[0023] An amount of commercially purchased deuterium oxide-depleted water (2-3 ppm deuterium) as a tracer is introduced, as a component of a drilling mud, into a subterranean formation via a well-bore. A sponge core sample is then taken from the subterranean formation adjacent to the well-bore using conventional sponge coring techniques and equipment. This sample is taken at an appropriate point in time after introduction of the deuterium oxide-depleted water, such that at least a portion of the deuterium oxide-depleted water would likely have had time to migrate to the region of the core sample, assuming such migration is possible. The sponge core is then extracted to the surface, and the sponge liners appropriately preserved to ensure retention of any fluids absorbed therein. The fluids are then removed from the sponge liners corresponding to one specific core location by means of a Dean and Stark apparatus. The fluids are analyzed for the presence of deuterium using conventional gas-chromatographic-mass spectrophotometric equipment and techniques. From this analysis it is determined that the deuterium concentration of the fluid in the core at this location is only about 10 ppm. From this it may be inferred that a large proportion of the tracer has migrated to this location within the allocated time. From this information the permeability of the formation may then be estimated.

What is claimed is:

1. A method of ascertaining or measuring an event comprising using deuterium oxide-depleted water as a tracer.

2. The method of claim 1 wherein the event being ascertained or measured occurs in a subterranean formation.

3. The method of claim 2 wherein the event is fluid migration.

4. The method of claim 3 wherein the fluid migration indicates a property of a subterranean formation.

5. The method of claim 4 wherein the property is the porosity, permeability or fluids saturation of the subterranean formation.

6. The method of claim 5 wherein the subterranean formation is being drilled for recovery of oil or gas.

7. A method of ascertaining or measuring a subterranean event comprising

transporting deuterium oxide-depleted water, as a tracer, to a first subterranean location;

allowing a time period sufficient for the tracer to migrate to a second subterranean location, assuming such migration is possible; and

using a tracer detection means or method to measure such tracer in the second subterranean location.

8. The method of claim 7 wherein the first subterranean location is a well-bore, the second subterranean location is a subterranean formation, and the tracer detection means or method includes obtaining a core sample from the subterranean formation.

9. The method of claim 8 wherein the tracer detection means or method is selected from the group consisting of mass spectrophotometry, gas chromatography-mass spectrophotometry, HPLC mass spectrophotometry, and nuclear magnetic resonance (NMR) imaging.

10. The method of claim 8 wherein the core sample is a sponge core.

11. The method of claim 7 wherein the second subterranean location is a subterranean formation and the measurement of tracer in the subterranean formation is used to determine a property of the subterranean formation.

12. The method of claim 11 wherein the property is porosity, permeability or fluids saturation.

13. A method of ascertaining or measuring filtrate contamination of a subterranean formation comprising

transporting deuterium oxide-depleted water, as a tracer, to a downhole location having adjacent thereto a subterranean formation wherein fluid is located;

allowing a time sufficient for the tracer to infiltrate the adjacent subterranean formation, assuming such infiltration is possible;

obtaining a sample of the subterranean formation such that the fluid therein is preserved; and

measuring the amount of tracer in the fluid.

14. The method of claim 13 wherein the sample of the subterranean formation is a sponge core sample.

15. The method of claim 14 further comprising extracting the fluid from the sponge core sample by means of retort distillation or use of a Dean and Stark apparatus.

16. The method of claim 13 wherein a tracer detection means or method, selected from the group consisting of mass spectrophotometry, gas chromatograph-mass spectrophotometry, HPLC mass spectrophotometry, and nuclear magnetic resonance (NMR) imaging, is used to measure the amount of tracer in the fluid.

17. The method of claim 13 wherein the amount of the tracer in the fluid is used to determine a property of the subterranean formation.

18. The method of claim 17 wherein the property is porosity, permeability or fluids saturation.

19. The method of claim 13 further comprising transporting a second tracer.

20. The method of claim 18 wherein the second tracer is tritium.

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