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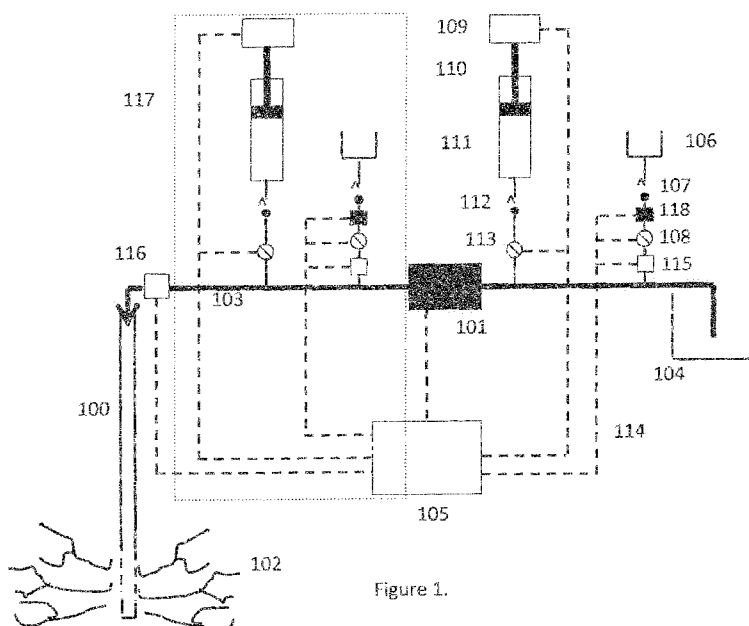


Figure 1.

(57) Abstract: A tracer particle for use in the exploration, production, transportation and/or storage of oil and/or gas, the tracer particle comprising a proppant material, a coating layer at least partially surrounding the proppant material and a tracer material within the coating layer, the tracer material having an identifiable DNA. There is also disclosed a tracer nanoparticle for use in the exploration, production, transportation and/or storage of oil and/or gas, the tracer nanoparticle comprising a tracer material having an identifiable DNA, and at least one chemical moiety located in at least an outer surface of the tracer nanoparticle, the at least one chemical moiety comprising at least one protein, at least one antibody, and/or at least one hydroxyl moiety. Methods and apparatus of tracing fluid during the exploration, production, transport and/or storage of oil and/or gas are also disclosed.



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Fluid Identification System

The present invention relates to a particle capture and sampling system, a method of particle capture and sampling system. In particular, this invention relates to a tracer technology and the applications thereof within the oil and gas exploration, production and transportation industries.

Many different fluids are introduced, produced or moved during the oil and gas operations of exploration, production and transportation. These fluids range from those manufactured to perform specific functions to those collected from different formations in a well. Some of the fluids collected are fluids originally injected into the well or reservoir rocks, returning to the surface during operations such as drilling mud or fracturing fluids. Other fluids that are used occur naturally in the formation rocks, for example, oil, gas condensate and water. Of course, in many cases fluids collected can be a mixture of naturally occurring fluids and fluids introduced in to reservoir rocks.

During the life of a well or oil field many different kinds of fluids are used and a lot will be returned during production. It is important to understand how the fluids that are injected move through the 'system', which consists both of the reservoir rocks and the wells that are drilled into the formation. The information gleaned from this understanding can tell the operator (for example, the oil company managing the field) a lot about the efficiency of production of oil and gas, how well certain specialised fluids are working, e.g., stimulation fluids, whether fluids are moving from one production zone to another (for example, through the reservoir rock or behinds seals in a well that are meant to isolate these zones) and also if some of the fluids injected are finding a route into shallower aquifers which could lead to environmental issues.

In particular, there are growing concerns that recent significant fracturing operations in shale gas formations create fracture paths where fracturing or stimulation fluids or naturally occurring formation fluids/gases flow into nearby aquifers. Early identification or confirmation that such flow is not occurring would be of significant value to the operator and society in general. In addition a better understanding of

these fluid flows can allow the operator to change or adjust the production strategies in order to improve the overall productivity of the field.

As an example, it is a common practice during the later production phases of a field to inject water (or other fluids or gases) into a reservoir formation through one or more wells in the field, in order to 'sweep' the remaining oil in the reservoir formation towards the producing wells. This is one technique of a range collectively called enhanced oil recovery (EOR) methods.

However, if a lot of the injected water is flowing through natural fractures or faults into a different reservoir formation then the efficiency of the 'sweep' can be much reduced. Understanding these issues early can allow the operator to change the EOR strategy (e.g., try to seal the fractures or switch injection into a different reservoir formation) in order to improve the field productivity. The ability to detect and understand these issues early has significant value for the operator.

However, it should be understood that during the life of a field, a significant number of different fluids are used and the system can be very complex since it involves the reservoir rocks, both naturally occurring and operation induced fractures, faults, and the collection of wells that are drilled through overlying rock formations into the reservoir rocks. Therefore the tracking of these fluids is very complex and requires technology not presently available today.

A common practice that is used today to try and understand fluid flow is to use what is called a tracer. In general the tracer is added to a fluid at one point in the process and is detected at another point later in the process. For example, it is common to add a tracer to the drilling mud and to detect it in the mud that returns to the surface. If the time the tracer is added and the time it is first detected in the returns are compared then the fluid circulation time can be easily calculated as the difference between the two. This circulation time can help establish if the well is being cleaned properly or if the hole drilled is in gauge, washed out or has other potential flow paths.

There exist several tracer technologies used in the oil and gas business today. Generally they can be categorized into three types:

- 1) A nonreactive, easily differentiated material placed in the mud circulating system at a certain time to be identified when it returns to surface. Mud tracers are used to determine circulation time. Dyes, paints, glitter or any material that will follow the mud can be used.
- 2) A chemical or isotopic marker that is uniformly distributed in the continuous phase of a drilling, coring or completion fluid and used to later identify the filtrate in cores or in fluids sampled from the reservoir. The tracer must become part of the filtrate, remaining in solution and moving with the filtrate into permeable zones. It should not be absorbed on clays or degrade. It needs to be measureable in trace amounts and safe to handle. Examples include: Weakly emitting radioisotopes which can be safe and effective, Bromide or iodide compounds are practical because they do not occur naturally in most muds or reservoirs and Nitrate anion added as sodium, potassium or calcium nitrate is one of the earliest tracers but it is difficult to analyse and degradation can be significant.
- 3) Radioactive 'paints' applied to a specific part of the borehole so that a particular zone can be precisely identified upon re-entry into the borehole.

The application of the first two of these methods is limited in that they generally provide a single tracer (the third does not apply to circulating fluids). That is, it can be difficult or impossible to tag multiple fluids and differentiate between them. Long-term events such as detection of injected water from offset injection wells are very difficult due to degradation of the tracer with time. As a result, Mathematical modelling is still the primary method of estimating (quantifying) the flow of different fluids within the reservoir or between different reservoir horizons, for example, through fractures or faults etc. However, these models require many assumptions, which results in a broad range of possible outcomes.

In addition, it is important to introduce the tracer material into the system in a controlled fashion that takes into account the application for which it is to be used. If the application is to monitor the flow-back of fracturing fluids from a multistage fracturing operation then it is important to inject different and unique tracers at the same time as the fracturing fluid is changed for each fracturing stage. If this is not carried out correctly then it is possible to misinterpret the results as different tracers

are detected in the returning fluids. In some operations materials are pumped into the well to perform various functions, for example, propping open a fracture or filtering sand from production fluids to prevent it reaching the surface where it can cause wear to equipment. It would be desirable to use these materials as a means to transport tracers into the well so that injection of such tracers did not require an additional step. In addition, the collection of representative samples can be a difficult and manually intensive exercise. For example, many samples can be taken which do not show signs of the tracer material but this could be because the time at which the sample was taken just happens to miss the returning tracer material. If a sample was taken just a little earlier or just a little later then the tracer material may well have been detected. Such misses can result in incorrect interpretation of the system behaviour. Ideally sampling would be automatic and continuous. If it was also controlled in a coordinated manner with the tracer injection profile (that is, concentrations as a function of time) then more information about the tracer transit through the system (e.g., the well(s) and/or formation) can be gleaned by comparing the two profiles, for example, the time between the peaks of the injection and detection profiles will give the transit time and the change in the width of the injection profile compared to the width of the detection profile will provide information about the particle dispersion within the system.

GB2489714 and WO2012136734 disclose a system and method that uses encapsulated DNA in nanoparticles for unique fluid identification. These patents also disclose methods for introducing and capturing the nanoparticles as they are returned entrained in the flow of fluids from the well or are captured by taking samples from the well or reservoir. The method of pumping the particles entrained in the fluids to be traced is disclosed. While these approaches will work in many situations, they are not optimal in others.

This invention addresses the limitations of the technology presently used and disclosed in the prior art.

The present inventors have worked to establish technical solutions to the above restrictions associated with technology presently used in the industry or disclosed in the prior art.

The present invention accordingly provides apparatus and methods for the controlled introduction of DNA nano or micro particles in to the flow system and their capture as the leave the flow system. Here we define the flow system as an oil and gas well or a series of wells or a reservoir or any sub-surface rock formation or a pipeline network used to transport oil and gas or any combination of the above.

Preferred aspects of the invention relate to the introduction, detection, collection and separation of nanoparticles in the continuous phase of fluids that are used within the oil and gas industry. The application of controlled introduction and capture of these nanoparticles for the better understanding of reservoir and sub-surface fluid flow and also the movement of fluids within a well, for example, from one formation to another or from one well section to another or from fractures generated in the formation and the well or between wells (e.g. during injection operations) are some of the embodiments described in this invention.

In a first aspect, the present invention provides a tracer particle for use in the exploration, production, transportation and/or storage of oil and/or gas, the tracer particle comprising a proppant material, a coating layer at least partially surrounding the proppant material and a tracer material within the coating layer, the tracer material having an identifiable DNA.

Optionally, the proppant material comprises sand particles, gravel particles, synthetic ceramic materials, or any mixture thereof.

Optionally, the tracer material comprises a plurality of nanoparticles having identifiable DNA dispersed within the coating layer.

Optionally, an outer surface of at least some of the nanoparticles is functionalised for capture by a physical or chemical mechanism. Typically, the outer surface of at least some of the nanoparticles is chemically functionalised for capture by a chemical mechanism. The outer surface of at least some of the nanoparticles may comprise at least one protein, at least one antibody, and/or at least one hydroxyl moiety, located in at least an outer surface of the coating layer. The at least one protein may comprise streptavidin, biotin, protein A or any mixture thereof, the at least one antibody may comprise an immunoglobulin G antibody, and/or the at least one hydroxyl moiety

may be present in at least one of a diol or *cis*-diol moiety and an alpha-hydroxy acid moiety or a mixture thereof.

Optionally, the identifiable DNA is complexed with a complexing agent, for example as a complexing polymer. The identifiable DNA may be at least partly encapsulated by an encapsulating polymer, for example the encapsulating polymer comprising at least one acrylate-, methacrylate- or styrene-based polymer. The encapsulating polymer may be a cross-linked polymer including a cross-linker, optionally the cross-linker being adapted to be chemically reduced by a reducing agent thereby to degrade the encapsulating polymer to release the DNA for analysis, further optionally a disulfide cross-linker. These embodiments are disclosed in further detail in WO2012136734, the disclosures of which, concerning at least the complexing polymer and the encapsulating polymer, are incorporated herein by reference.

Optionally, the coating layer comprises an oil-soluble or water-soluble material. The oil-soluble material may be selected from a hydrocarbon wax, a resin, a polymer or any mixture of two or more thereof. The water-soluble material may be at least one polymer, typically the at least one polymer comprising polylactic acid, partially hydrolysed polyacrylamide, polyethylene oxide or any mixture of two or more thereof.

There is also provided a tracer sample comprising a plurality of tracer particles according to the invention, the tracer particles comprising a mixture of a plurality of first tracer particles and a plurality of second tracer particles, the first tracer particles comprising a first tracer material and the second tracer particles comprising a second tracer material, wherein the first and second tracer materials have different identifiable DNA, and the coating layers of the first and second tracer particles comprise respective first and second oil-soluble and/or water-soluble material which have respective different solubility in oil and/or water. The coating layer of the first tracer particles may comprise an oil-soluble material and the coating layer of the second tracer particles may comprise a water-soluble material.

With respect to the first aspect, optionally the coating layer is an inner coating layer with a first tracer material therein, and the tracer particle further comprises an outer coating layer at least partially surrounding the inner coating layer and a second tracer material within the outer coating layer, wherein the first and second tracer materials

have different identifiable DNA and the inner and outer coating layers comprise respective first and second oil-soluble and/or water-soluble material which have respective different solubility in oil and/or water. The outer coating layer may comprise an oil-soluble material and the inner coating layer comprises a water-soluble material. The oil-soluble material may be selected from a hydrocarbon wax, a resin, a polymer or any mixture of two or more thereof. The water-soluble material may be at least one polymer, for example the at least one polymer comprising polylactic acid, partially hydrolysed polyacrylamide, polyethylene oxide or any mixture of two or more thereof.

In a second aspect, the present invention provides a tracer particle in the form of a capsule comprising an outer shell encapsulating tracer material which comprises a plurality of nanoparticles having identifiable DNA.

Optionally, an outer surface of at least some of the nanoparticles is functionalised for capture by a physical or chemical mechanism. Typically, the outer surface of at least some of the nanoparticles is chemically functionalised for capture by a chemical mechanism. The outer surface of at least some of the nanoparticles may comprise at least one protein, at least one antibody, and/or at least one hydroxyl moiety, located in at least an outer surface of the coating layer. The at least one protein may comprise streptavidin, biotin, protein A or any mixture thereof, the at least one antibody may comprise an immunoglobulin G antibody, and/or the at least one hydroxyl moiety may be present in at least one of a diol or *cis*-diol moiety and an alpha-hydroxy acid moiety or a mixture thereof.

Optionally, the identifiable DNA is complexed with a complexing agent. The complexing agent may be a complexing polymer. The identifiable DNA may be at least partly encapsulated by an encapsulating polymer. The encapsulating polymer may comprise at least one acrylate-, methacrylate- or styrene-based polymer. Typically, the encapsulating polymer is a cross-linked polymer including a cross-linker, optionally wherein the cross-linker is adapted to be chemically reduced by a reducing agent thereby to degrade the encapsulating polymer to release the DNA for analysis, further optionally a disulfide cross-linker.

Optionally, the outer shell comprises at least one cellulose material, further optionally hydrocellulose.

The invention also provides a plurality of tracer particles according to the invention or a tracer sample according to the invention, wherein the tracer particles are present in a carrier fluid which comprises a detectable indicator, optionally comprising at least one dye, in addition to the tracer material.

In a third aspect, the present invention provides a method of tracing fluid during the exploration, production and/or storage of oil and/or gas, the method comprising the steps of:

- (i) providing a tracer particle comprising (a) a proppant material, a coating layer at least partially surrounding the proppant material and a tracer material within the coating layer, the tracer material having an identifiable DNA or (b) a capsule comprising an outer shell encapsulating tracer material which comprises a plurality of nanoparticles having identifiable DNA;
- (ii) introducing the tracer particle into a fluid;
- (iii) injecting the fluid, containing the tracer particle therein, into a supply of oil or gas;
- (iv) subsequently recovering at least some of the tracer material which was in the injected fluid; and
- (v) analyzing any identifiable DNA in the tracer material.

Optionally, in step (iii) the fluid is injected, either as a pulse or continuously, into a flow of a second fluid which may or may not contain a proppant. Optionally, in step (iii) the fluid is injected as a sequence of intermittent pulses.

Optionally, a plurality of the oil or gas wells is provided, and in step (iii) a respective sample of the fluid is injected as a respective pulse into a respective well or at least two of the respective wells, and optionally in preceding or subsequent injection operations a pulse of a further tracer material comprising a plurality of nanoparticles having an identifiable DNA and in the absence of proppant material is injected into the respective well or at least two of the respective wells.

Optionally, in step (iii) the fluid is injected sequentially into the at least two of the respective wells.

Optionally, in step (iii) an injection time that the fluid is injected is recorded and in step (iv) a recovery time that the tracer material is recovered is recorded. Typically, a residence time between the injection and recovery times is determined. The residence time may be input as a parameter into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof. The parameter may be adapted to function as a calibration parameter for the computer model.

Optionally, in step (iii) an injection time period during which the fluid is injected is recorded and in step (iv) a recovery time period during which the tracer material is recovered is recorded. Typically, a time period relationship between the injection time period and the recovery time period is determined. A variation of the time period relationship with time may be determined. Optionally, at least one of the time period relationship or the variation of the time period relationship with time is input as a parameter, optionally as a calibration parameter, into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.

Optionally, in step (iii) in a first injection operation a first tracer material is injected and subsequently in a second injection operation a second tracer material, optionally in the presence or absence of proppant material, is injected, the first and second tracer materials having different identifiable DNA.

Optionally, in step (iii) the injected fluid comprises a known initial concentration of the tracer material and in step (iv) a final concentration of the recovered tracer material is recorded. Typically, in step (iii) the known initial concentration of the tracer material varies with time and in step (iv) a final concentration, varying with time, of the recovered tracer material is recorded. A concentration relationship between the initial and final concentrations may be determined. A variation of the concentration relationship with time may be determined. Optionally, at least one of the concentration relationship or the variation of the concentration relationship with time is input as a parameter into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.

Optionally, in step (iii) the fluid comprises a detectable indicator in addition to the tracer material. The detectable indicator may comprise at least one dye.

Optionally, in step (iii) the fluid is injected into an oil or gas well in a hydraulic fracturing operation. During the hydraulic fracturing operation the coating layer may be degraded, such as by dissolution and/or breaking, within the well to release the tracer material into the well.

The method may optionally further comprise the step of injecting into the respective well or at least two of the respective wells a pulse of a further tracer material comprising a plurality of nanoparticles having an identifiable DNA and in the absence of proppant material in an enhanced oil recover (EOR) operation. Optionally, a plurality of the oil or gas wells is provided defining a central area therebetween, and in step (iii) a respective sample of the fluid is injected into a respective well or at least two of the respective wells, each sample having a respective tracer material therein.

Optionally, in step (ii) the tracer particle is introduced into the fluid after the fluid has been pressurized to an injection pressure. In step (ii) the injection pressure may be controlled or varied to control or vary the injection rate in step (iii).

Optionally, in step (ii) a plurality of the tracer particles are introduced into the fluid at a known concentration and/or at a known dosage rate and/or over a known time period.

Optionally, the supply of oil or gas is monitored to detect the fluid, any nanoparticles having an identifiable DNA therein or any identifiable DNA therein, and step (iv) is initiated after detection of the fluid or any nanoparticles having the identifiable DNA or any identifiable DNA in the supply of oil or gas. The monitoring of the supply of oil or gas may include measuring a physical property of the fluid or any tracer material therein, the physical property being selected from absorption and/or reflection and/or scattering of electromagnetic radiation, dielectric constant, colour in the visible region of the spectrum, and fluorescence, or any combination thereof.

Optionally, in step (iv) the tracer material is captured on a surface of a recovery element, the surface being adapted to bind chemically or physically to a surface of the tracer material. Typically, the tracer material comprises a plurality of nanoparticles having identifiable DNA.

Optionally, the surface of the recovery element includes a first chemical moiety adapted to bind chemically to a complementary second chemical moiety on the

surface of the tracer nanoparticle. The first or second chemical moiety may comprise at least one of a boron acid or a derivative thereof, for example phenylboronic acid or benzoboroxole or a mixture thereof. The first or second chemical moiety may comprise at least one hydroxyl moiety, for example the at least one hydroxyl moiety being present in at least one of a diol or *cis*-diol moiety and an alpha-hydroxy acid moiety or a mixture thereof. The first or second chemical moiety may comprise at least one protein, for example streptavidin, biotin, protein A or any mixture thereof. The first or second chemical moiety may comprise at least one antibody, for example an immunoglobulin G antibody.

Optionally, the surface of the recovery element is monitored to indicate, directly or indirectly, capture of the nanoparticle on the surface of the recovery element. Typically, the electrical properties or visual appearance of the surface of the recovery element is monitored. Optionally, the surface of the recovery element is monitored to indicate, directly or indirectly, an amount of the nanoparticle captured on the surface of the recovery element. Typically, the indicated amount of the nanoparticle captured on the surface of the recovery element reaches a predetermined threshold, the analysis step (v) is initiated for the nanoparticle captured on the surface of the recovery element.

Optionally, in step (iii) a predetermined volume of the fluid, having a predetermined concentration of the identifiable DNA, is injected. In step (iii) the predetermined volume of the fluid may be injected from a cartridge containing the predetermined volume, may be injected by a plunger mechanism or may be injected from a tank through a flowmeter.

Optionally, the proppant material comprises sand particles, gravel particles, synthetic ceramic materials or any mixture thereof.

Optionally, the tracer material comprises a plurality of nanoparticles having identifiable DNA dispersed within the coating layer.

Optionally, an outer surface of at least some of the nanoparticles is functionalised for capture by a physical or chemical mechanism. Typically, the outer surface of at least some of the nanoparticles is chemically functionalised for capture by a chemical mechanism. The outer surface of at least some of the nanoparticles may comprise at

least one protein, at least one antibody, and/or at least one hydroxyl moiety, located in at least an outer surface of the nanoparticle. Optionally, the at least one protein comprises streptavidin, biotin, protein A or any mixture thereof, the at least one antibody comprises an immunoglobulin G antibody, and/or the at least one hydroxyl moiety is present in at least one of a diol or *cis*-diol moiety and an alpha-hydroxy acid moiety or a mixture thereof.

Optionally, the coating layer comprises an oil-soluble or water-soluble material. The oil-soluble material may be selected from a hydrocarbon wax, a resin, a polymer or any mixture of two or more thereof. The oil-soluble material may at least partly dissolve in at least one hydrocarbon present in the oil or gas well. The water-soluble material may be at least one polymer, for example the at least one polymer comprising polylactic acid, partially hydrolysed polyacrylamide, polyethylene oxide or any mixture of two or more thereof. The water-soluble material may at least partly dissolve in at least one aqueous liquid present in the oil or gas well.

Optionally, in step (iii) a plurality of tracer particles is injected, the tracer particles comprising a mixture of a plurality of first tracer particles and a plurality of second tracer particles, the first tracer particles comprising a first tracer material and the second tracer particles comprising a second tracer material, wherein the first and second tracer materials have different identifiable DNA, and the coating layers of the first and second tracer particles comprise respective first and second oil-soluble and/or water-soluble material which have respective different solubility in oil and/or water. Further optionally, the coating layer of the first tracer particles comprises an oil-soluble material and the coating layer of the second tracer particles comprises a water-soluble material.

Optionally, the coating layer is an inner coating layer with a first tracer material therein, and the tracer particle further comprises an outer coating layer at least partially surrounding the inner coating layer and a second tracer material within the outer coating layer, wherein the first and second tracer materials have different identifiable DNA and the inner and outer coating layers comprise respective first and second oil-soluble and/or water-soluble material which have respective different solubility in oil and/or water. The outer coating layer may comprise an oil-soluble material and the inner coating layer may comprise a water-soluble material. The oil-

soluble material may be selected from a hydrocarbon wax, a resin, a polymer or any mixture of two or more thereof. The water-soluble material may be at least one polymer, for example the at least one polymer comprising polylactic acid, partially hydrolysed polyacrylamide, polyethylene oxide or any mixture of two or more thereof.

Optionally, the outer shell comprises a cellulose material, further optionally hydrocellulose. Optionally, the outer shell fractures under compression within an oil or gas well to release the nanoparticles encapsulated therein into the oil or gas well.

In a fourth aspect, the present invention provides an apparatus for tracing fluid during the exploration, production, transportation and/or storage of oil and/or gas, the apparatus comprising an injector unit for injecting a pulse of fluid, containing at least one tracer particle, including tracer material having identifiable DNA, therein, into a supply of oil or gas; a monitoring unit for monitoring the supply of oil or gas to detect the fluid or any tracer material therein; a recovery unit for subsequently recovering at least some of the tracer material which was in the injected fluid, the recovery unit includes a recovery element having a surface adapted to bind chemically or physically to a surface of the tracer material to capture the tracer material on the recovery element; an analysis unit for analyzing any identifiable DNA in the tracer material, and a controller for controlling the operation of at least one of the injector unit, the monitoring unit, the recovery unit and the analysis unit or any combination thereof.

Optionally, the injector unit is adapted to inject the fluid as a sequence of intermittent pulses.

Optionally, the controller is adapted to record an injection time that the fluid is injected by the injector unit and a recovery time that the tracer material is recovered by the recovery unit. The controller may be adapted to determine a residence time between the injection and recovery times. The controller may be adapted to input the residence time as a parameter, optionally a calibration parameter into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.

Optionally, the controller is adapted to record an injection time period during which the fluid is injected by the injector unit and a recovery time period during which the

tracer material is recovered by the recovery unit. The controller may be adapted to determine a time period relationship between the injection time period and the recovery time period. The controller may be adapted to determine a variation of the time period relationship with time. The controller may be adapted to input at least one of the time period relationship or the variation of the time period relationship with time as a parameter, optionally a calibration parameter, into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.

Optionally, the controller is adapted to record a concentration of the tracer material injected by the injector unit and/or recovered by the recovery unit. The controller may be adapted to determine a concentration relationship between the concentration of the tracer material injected by the injector unit and the concentration of the tracer material recovered by the recovery unit. The controller may be adapted to determine a variation of the concentration relationship with time. The controller may be adapted to input at least one of the concentration relationship or the variation of the concentration relationship with time as a parameter, optionally a calibration parameter, into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.

Optionally, the monitoring unit includes a measuring device for measuring a physical property of the fluid or any tracer material therein, the physical property being selected from absorption and/or reflection and/or scattering of electromagnetic radiation, dielectric constant, colour in the visible region of the spectrum, and fluorescence, or any combination thereof.

Optionally, the surface of the recovery element includes a first chemical moiety adapted to bind chemically to a complementary second chemical moiety on the surface of the tracer material. The first chemical moiety may comprise at least one of a boron acid or a derivative thereof, for example phenylboronic acid or benzoboroxole or a mixture thereof. The first chemical moiety may comprise at least one protein, for example streptavidin, biotin, protein A or any mixture thereof. The first chemical moiety may comprise at least one antibody, for example an immunoglobulin G antibody.

Optionally, the monitoring unit is adapted to monitor the surface of the recovery element to indicate, directly or indirectly, capture of the tracer material on the surface of the recovery element. The monitoring unit may be adapted to monitor electrical properties or visual appearance of the surface of the recovery element. The monitoring unit may be adapted to monitor the surface of the recovery element to indicate, directly or indirectly, an amount of the tracer material captured on the surface of the recovery element. The controller may be adapted to initiate the analysis unit to analyse the tracer material captured on the surface of the recovery element after an indicated amount of the tracer material captured on the surface of the recovery element reaches a predetermined threshold.

Optionally, the injector unit is adapted to inject a predetermined volume of the fluid is injected. The injector unit may be adapted to inject the predetermined volume of the fluid from a cartridge containing the predetermined volume. The injector unit may be adapted to inject the predetermined volume of the fluid by a plunger mechanism. The injector unit may be adapted to inject the predetermined volume of the fluid from a tank through a flowmeter.

In a fifth aspect, the present invention provides a tracer nanoparticle for use in the exploration, production, transportation and/or storage of oil and/or gas, the tracer nanoparticle comprising a tracer material having an identifiable DNA, and at least one chemical moiety located in at least an outer surface of the tracer nanoparticle, the at least one chemical moiety comprising at least one protein, at least one antibody, and/or at least one hydroxyl moiety.

The at least one protein may comprise streptavidin, biotin, protein A or any mixture thereof. The at least one antibody may comprise an immunoglobulin G antibody. The at least one hydroxyl moiety may be present in at least one of a diol or *cis*-diol moiety and an alpha-hydroxy acid moiety or a mixture thereof.

Optionally, the identifiable DNA is complexed with a complexing agent, optionally wherein the complexing agent is a complexing polymer. Optionally, the identifiable DNA is at least partly encapsulated by an encapsulating polymer, optionally wherein the encapsulating polymer comprises at least one acrylate-, methacrylate- or styrene-based polymer, further optionally wherein the encapsulating polymer is a cross-linked polymer including a cross-linker, yet further optionally wherein the cross-linker is

adapted to be chemically reduced by a reducing agent thereby to degrade the encapsulating polymer to release the DNA for analysis, optionally a disulfide cross-linker.

There is also provided a tracer particle having an outer surface which is provided by a coating layer of an oil-soluble or water-soluble material which encapsulates a plurality of the nanoparticles according to the fifth aspect of the present invention.

Optionally, the tracer particle further comprises a proppant material at least partly surrounded by the coating layer, optionally wherein the proppant material comprises a sand particle, a gravel particle, a synthetic ceramic material, or any mixture thereof.

There is also provided a tracer sample comprising a plurality of tracer particles according to claim 144 or claim 145, the tracer particles comprising a mixture of a plurality of first tracer particles and a plurality of second tracer particles, the first tracer particles comprising a first tracer material and the second tracer particles comprising a second tracer material, wherein the first and second tracer materials have different identifiable DNA, and the coating layers of the first and second tracer particles comprise respective first and second oil-soluble and/or water-soluble material which have respective different solubility in oil and/or water.

Optionally, the coating layer of the first tracer particles comprises an oil-soluble material and the coating layer of the second tracer particles comprises a water-soluble material.

Optionally, the coating layer is an inner coating layer with a first tracer material therein, and the tracer particle further comprises an outer coating layer at least partially surrounding the inner coating layer and a second tracer material within the outer coating layer, wherein the first and second tracer materials have different identifiable DNA and the inner and outer coating layers comprise respective first and second oil-soluble and/or water-soluble material which have respective different solubility in oil and/or water. Optionally, the outer coating layer comprises an oil-soluble material and the inner coating layer comprises a water-soluble material.

Optionally, the oil-soluble material is selected from a hydrocarbon wax, a resin, a polymer or any mixture of two or more thereof. Optionally, the water-soluble material is at least one polymer. Optionally, the at least one polymer comprises polylactic acid,

partially hydrolysed polyacrylamide, polyethylene oxide or any mixture of two or more thereof.

In a sixth aspect, the present invention provides a method of tracing fluid during the exploration, production, transportation and/or storage of oil and/or gas, the method comprising the steps of:

- (i) providing tracer nanoparticles comprising a tracer material having an identifiable DNA, and at least one chemical moiety located in at least an outer surface of the tracer nanoparticles;
- (ii) introducing the tracer nanoparticles into a fluid;
- (iii) injecting the fluid, containing the tracer nanoparticles therein, into a supply of oil or gas;
- (iv) subsequently recovering at least some of the tracer material which was in the injected fluid, wherein in step (iv) the tracer material is captured on a surface of a recovery element, the surface being adapted to bind chemically or physically to the at least one chemical moiety; and
- (v) analyzing any identifiable DNA in the tracer material.

Optionally, the surface of the recovery element includes a first chemical moiety adapted to bind chemically to a complementary second chemical moiety located in at least the outer surface of the tracer nanoparticle. The first or second chemical moiety may comprise at least one of a boron acid or a derivative thereof, for example phenylboronic acid or benzoboroxole or a mixture thereof. The first or second chemical moiety may comprise at least one hydroxyl moiety, for example the at least one hydroxyl moiety is present in at least one of a diol or *cis*-diol moiety and an alpha-hydroxy acid moiety or a mixture thereof. The first or second chemical moiety may comprise at least one protein, for example streptavidin, biotin, protein A or any mixture thereof. The first or second chemical moiety may comprise at least one antibody, for example an immunoglobulin G antibody.

Optionally, the surface of the recovery element is monitored to indicate, directly or indirectly, capture of the tracer nanoparticle on the surface of the recovery element. The electrical properties or visual appearance of the surface of the recovery element may be monitored.

Optionally, the surface of the recovery element is monitored to indicate, directly or indirectly, an amount of the tracer nanoparticles captured on the surface of the recovery element. When the indicated amount of the tracer nanoparticles captured on the surface of the recovery element reaches a predetermined threshold, the analysis step (v) may be initiated for the tracer nanoparticles captured on the surface of the recovery element.

In a seventh aspect, the present invention provides a method of tracing fluid during the exploration or production of oil and/or gas, the method comprising the steps of:

- (i) providing a tracer particle comprising a tracer material, the tracer material having an identifiable DNA;
- (ii) introducing the tracer particle into a fluid;
- (iii) injecting the fluid, containing the tracer particle therein, into a supply of oil or gas, and recording an injection parameter;
- (iv) subsequently recovering at least some of the tracer material which was in the injected fluid, and recording a recovery parameter;
- (v) analyzing any identifiable DNA in the tracer material; and
- (vi) before, simultaneously with, or after step (v), comparing the injection and recovery parameters to determine a property of the oil or gas reservoir and/or well and/or a property of the behaviour of the tracer particle or tracer material within the oil or gas reservoir and/or well.

Optionally, in step (iii) the injection parameter has a first variable and in step (iv) the recovery parameter has a second variable, and in step (vi) the first and second variables are compared.

Optionally, in step (iii) the fluid is injected as a pulse. Optionally, in step (iii) the fluid is injected as a sequence of intermittent pulses.

Optionally, a plurality of the oil or gas wells is provided, and in step (iii) a respective sample of the fluid is injected as a respective pulse into a respective well of at least two of the respective wells. In step (iii) the fluid may be injected sequentially into the at least two of the respective wells.

Optionally, in step (iii) an injection time that the fluid is injected is recorded and in step (iv) a recovery time that the tracer material is recovered is recorded. A residence time between the injection and recovery times may be determined. The residence time may be input as a parameter, optionally a calibration parameter, into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.

Optionally, in step (iii) an injection time period during which the fluid is injected is recorded and in step (iv) a recovery time period during which the tracer material is recovered is recorded. A time period relationship between the injection time period and the recovery time period may be determined. A variation of the time period relationship with time may be determined. At least one of the time period relationship or the variation of the time period relationship with time may be input as a parameter into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.

Optionally, in step (iii) in a first injection operation a first tracer material is injected and subsequently in a second injection operation a second tracer material is injected, the first and second tracer materials having different identifiable DNA.

Optionally, in step (iii) the injected fluid comprises a known initial concentration of the tracer material and in step (iv) a final concentration of the recovered tracer material is recorded. In step (iii) the known initial concentration of the tracer material may vary with time and in step (iv) a final concentration, varying with time, of the recovered tracer material may be recorded. A concentration relationship between the initial and final concentrations may be determined. A variation of the concentration relationship with time may be determined. At least one of the concentration relationship or the variation of the concentration relationship with time may be input as a parameter, optionally a calibration parameter, into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.

In an eighth aspect, the present invention provides a method of tracing fluid during the exploration and/or production, of oil and/or gas, the method comprising the steps of:

- (i) providing a tracer particle encapsulating a tracer material, the tracer material having an identifiable DNA;
- (ii) introducing the tracer particle into a fluid;
- (iii) injecting the fluid, containing the tracer particle therein, into an oil or gas well in a hydraulic fracturing operation;
- (iv) releasing the encapsulated tracer material having identifiable DNA, by compression of the tracer particle, or at least partial dissolution of encapsulant encapsulating the tracer material, in a fracture within the oil or gas well;
- (v) subsequently recovering at least some of the tracer material which was in the injected fluid;
- (vi) analyzing any identifiable DNA in the tracer material; and
- (vii) before, simultaneously with, or after step (v), determining the fracture closure time by analysis of the period between the injection time in step (iii) and the recovery time in step (v).

Optionally, in step (iii) the fluid is injected as a pulse. Optionally, in step (iii) the fluid is injected as a sequence of intermittent pulses.

Optionally, a plurality of the oil or gas wells is provided, and in step (iii) a respective sample of the fluid is injected as a respective pulse into a respective well of at least two of the respective wells. In step (iii) the fluid may be injected sequentially into the at least two of the respective wells.

Optionally, in step (iii) an injection time that the fluid is injected is recorded and in step (iv) a recovery time that the tracer material is recovered is recorded. A residence time between the injection and recovery times may be determined. The residence time may be input as a parameter, optionally a calibration parameter, into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.

Optionally, in step (iii) an injection time period during which the fluid is injected is recorded and in step (iv) a recovery time period during which the tracer material is recovered is recorded. A time period relationship between the injection time period and the recovery time period may be determined. A variation of the time period relationship with time may be determined. At least one of the time period relationship

or the variation of the time period relationship with time may be input as a parameter, optionally a calibration parameter, into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.

Optionally, in step (iii) in a first injection operation a first tracer material is injected and subsequently in a second injection operation a second tracer material is injected, the first and second tracer materials having different identifiable DNA.

Optionally, in step (iii) the injected fluid comprises a known initial concentration of the tracer material and in step (iv) a final concentration of the recovered tracer material is recorded. Typically, in step (iii) the known initial concentration of the tracer material varies with time and in step (iv) a final concentration, varying with time, of the recovered tracer material is recorded. A concentration relationship between the initial and final concentrations may be determined. A variation of the concentration relationship with time may be determined. Typically, wherein at least one of the concentration relationship or the variation of the concentration relationship with time is input as a parameter, optionally a calibration parameter, into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.

Optionally, in step (iii) the fluid comprises a detectable indicator in addition to the tracer material. The detectable indicator may comprise at least one dye.

Optionally, the tracer material is encapsulated within a coating layer of the tracer particle and during the hydraulic fracturing operation the coating layer is degraded within the well to release the tracer material into the well. Typically, the tracer material is encapsulated as a plurality of nanoparticles within the coating layer and during the hydraulic fracturing operation the coating layer is degraded within the well to release the nanoparticles into the well.

Optionally, in step (iii) the fluid is injected into an oil or gas well in an enhanced oil recovery (EOR) operation. Typically, a plurality of the oil or gas wells is provided defining a central area therebetween, and in step (iii) a respective sample of the fluid is injected into a respective well of at least two of the respective wells, each sample having a respective tracer material therein.

Optionally, in the tracer particle the identifiable DNA is complexed with a complexing agent, for example a complexing polymer. The identifiable DNA may be at least partly encapsulated by an encapsulating polymer in a nanoparticle, for example the encapsulating polymer comprising at least one acrylate-, methacrylate- or styrene-based polymer. The encapsulating polymer may be a cross-linked polymer including a cross-linker, optionally the cross-linker is adapted to be chemically reduced by a reducing agent thereby to degrade the encapsulating polymer to release the DNA for analysis, optionally a disulfide cross-linker.

Various embodiments of the invention are now generally described.

According to a first embodiment of this invention, there is provided a means to introduce a known volume of fluid containing nanoparticles of a predefined concentration into fluids that are being pumped into a well. The particles can be introduced into the fluid flow on either the high pressure or preferably on the low pressure side of the pump.

According to a second embodiment of this invention, there is provided a means to introduce a known sample volume of fluid containing nanoparticles of a predefined concentration at a predefined rate or rate profile (varying concentration with time) into the fluids that are being pumped into a well. The particles can be introduced into the fluid flow on either the high pressure or preferably the low pressure side of the pump.

According to a third embodiment of this invention, the particle injection rate is controlled as a function of the pump rate of the fluid being injected into a well. In order, for example, to achieve a particular nanoparticle concentration per unit volume of fluid being pumped into the well or some other nanoparticle distribution characteristic.

According to a fourth embodiment of this invention, the nanoparticles are suspended and introduced in a carrier fluid that is readily detected when it returns from the well. The carrier fluid can be a dye or a fluid with a known fluorescence characteristic, for example, fluorescence under examination with UV light.

According to a fifth embodiment of this invention, a control unit is provided that monitors the pump rate and/or particle fluid injection rate and controls valves and particle introduction volume rates in a prescribed fashion in order to satisfy certain particle injection criteria, for example, particle concentration per unit volume of injected fluids.

According to a sixth embodiment of this invention, there is provided a means to coat materials that are pumped into a well during certain operations, for example, fracturing proppant or gravel during gravel packing or cement, with nanoparticles (or otherwise bind to or incorporate within such materials).

According to a seventh aspect of this invention, the coating or binding material is designed to dissolve or breakdown to release the nanoparticles from the surface of the proppant material, for example, when the said coating comes into contact with water flowing from the formation and the nanoparticles flow to surface entrained in the water flow.

According to an eighth aspect of this invention, the coating material is designed to dissolve or breakdown to release the nanoparticles from the surface of the proppant material, for example, when the said coating comes into contact with hydrocarbon flowing from the formation and the nanoparticles flow to surface entrained in the hydrocarbon flow.

According to a ninth aspect of this invention, the coating material is designed to dissolve or breakdown to release the nanoparticles from the surface of the proppant material, for example, when the said coating comes into contact with a fluid with a particular chemical characteristic, for example, of a particular pH or with a pH within a particular range or above or below a particular value. Those skilled in the art will appreciate that there are other chemical characteristics that can be used.

Additionally, for fracturing applications nanoparticles can be encapsulated/embedded in larger capsules whose crush strength is such that they readily break when compressed between the proppant on closure of the fracture (for example the hydrocellulosic materials used to encapsulate gel fluid breakers in fracturing operations). These capsules are placed within the fracture along with the proppant and

as the fracture closes, the compressive stresses created cause these materials to rupture and the encapsulated nanoparticles are released at the inception of the clean-up/flow back process.

According to the a tenth embodiment of this invention, there is provided a means to monitor the return flow from a well to detect the presence of nanoparticles and to use this detection to trigger the sampling of the return flow in order to capture some of those particles and release the embedded DNA for analysis. The positive detection can trigger the capture of a sample or trigger the capture of a sequence of samples.

According to an eleventh embodiment of this invention, the nanoparticles are detected by a characteristic signature of the absorption or reflection spectra when the returning fluid is interrogated with a particular source, for example, electromagnetic waves of particular wavelengths or X-rays or any other form of radiation, and the nanoparticles within the fluid give rise to a characteristic absorption or reflective response that is measured by an appropriate detection device, thus providing an indication of their presences or not. In another example inline mass spectrometry can also be used for this purpose or some of scattering characteristics of EM of different wavelength (e.g., light or X-rays) by the nanoparticles or monitoring the dielectric constant or any other physical property of the fluid changed by the presence of nanoparticles

According to a twelfth embodiment of this invention, there is provided a means to detect the presence of a specific carrier fluid in which the nanoparticles were introduced. As an example, this carrier fluid could be a dye that can be detected visually (by the human eye) or preferably automatically through the detection of its colour when interrogated with, e.g., white light. Or it could be a fluid that fluorescences when interrogated at a particular wavelength, for example, pic-green. Those skilled in the art will recognize that there are many other options and all are encompassed in this invention.

According to a thirteenth embodiment of this invention, there is provided a means to produce a nanoparticle comprising specific surface functionalities The surface functionalities are chemical groups that enable the nanoparticles to be concentrated when coming into contact with a chemically-complementary 'tab' (designed to enable

chemical or physical binding or absorption of the nanoparticles to the tab) placed in the flow coming from the well. As fluid flows/passes over the 'tab' or grid or solid support, nanoparticles in the flow stick to the tab and are thus separated from the fluid flow. To effectively bind the nanoparticles as they flow past, the tab must be functionalised with a moiety that specifically binds to the nanoparticle surface functional groups. One example of this approach would be to use a nanoparticle that comprises *cis*-diol or alpha-hydroxy acid groups protruding from the outer surface and a 'tab' that is coated with a boron acid moiety (e.g. phenylboronic acid, benzoboroxole etc). However, those skilled in the art will appreciate that other groups could provide the same technical effect (such as provision of a donor/receptor lock and key docking mechanism) and these are encompassed in this invention.

According to a fourteenth embodiment of this invention, there is provided a means to continually interrogate the tab in order to determine changes in its physical or electrical properties, for example, its resistance, that will change as the number of nanoparticles that are stuck on the tab increases. This measurement can thus be used to determine when the tab is fully loaded with captured nanoparticles and should be removed and replaced with a new tab. Other changes in the physical properties of the tab could equally be used to determine the particle loading on the tab, for example, its colour change as the number of captured particles increases.

According to a fifteenth embodiment of this invention, detection of changes in tab properties is used to trigger the capture of a sample or a sequence of samples of the fluid flowing out of the well.

According to a sixteenth embodiment of this invention, a controller is provided that monitors nanoparticle detection measurements and/or nanoparticle capture tabs and/or fluid flow rates, and uses this information to control valves and sample capture devices such that single or multiple samples are automatically taken and placed into sample bottles. The volume of each sample can be controlled. The rate at which the sample is taken can also be controlled in accordance with the returning fluid flow rate and/or the nanoparticle injection rate or injection profile so that representative samples are obtained. In addition, the time, volume, sample rate etc., can be recorded

for analysis with the injection parameters, in order to provide information about the nanoparticle transit through the flow system (well, reservoir etc).

According to a seventeenth embodiment of this invention, a magnetic component (eg an iron oxide) is incorporated into the tracer nanoparticle. This can be used (a) to detect the presence of nanoparticles in the return flow from the well by sensing changes in the magnetic characteristics (field) of the fluid and (b) to capture, separate and concentrate the nanoparticles for further analysis by passing the return fluid over a suitable magnet or through a magnetic separator.

Through these listed embodiments and aspects of this invention, the inventors have provided different embodiments, which cover some of the potential applications for the injection and capture of nanoparticles into oil & gas wells. However, it is understood that this is a subset of the potential applications and those skilled in the art will appreciate that there can be many others which are additionally envisaged in this invention.

Embodiment of the present invention will now be described by way of example only, with reference to the accompanying drawing, in which:

Figure 1 schematically illustrates several systems for the injection of fluids containing nanoparticles into a fracturing fluid pumped into a well.

Figures 2a, 2b and 2c schematically illustrate proppant particles coated with degradable material in which nanoparticles are embedded and are thus pumped into a well.

Figure 3 schematically shows a system for the detection of nanoparticles in the flow returning from a well and the collection of samples from such a flow.

Figure 4 schematically illustrates a tab that can be used to capture nanoparticles in the fluid returning from a well.

Figure 5 schematically illustrates nanoparticles with a functionalised surface coating and a particle collection tab that is 'chemically sticky' to the nanoparticles.

Figure 6 is an illustration of EOR as an example application.

In figures 1, 3, 4, and 5 solid lines represent flowlines and dashed lines represent measurement or control lines or cables. Also through out these embodiments, the inventors have used the example of fracturing a well by pumping fluids at high

pressures into the well. This operation is commonly referred to as ‘hydraulic fracturing’ or ‘fracking’ in the oil and gas industry. However, it will be appreciated by those skilled in the art that this invention can equally be applied where other fluids are injected into a well or reservoir for other purposes and where they may be later sampled, for example, water injection for the purposes of Enhanced Oil Recover (EOR) is one such application.

Hereinafter, the present invention will now be described in more detail with reference to the accompanying figures 1 to 6, in which exemplary embodiments of the invention are shown. The invention may, however, be embodied in many different forms and should not be construed as being limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the concept of the invention to those skilled in the art.

Referring to figure 1 where several systems to introduce or inject nanoparticles into a fluid flow that is being pumped into a well, 100, are shown. In this example, fracturing fluid is pumped into the well at high pressure in order to induce fractures in the formation, 102. The fracturing fluid is pumped by pump 101 from a tank 104, along a surface flowline 103. Optionally, there may be a flow meter 116 that measures the rate at which the fracturing fluid is pumped into the well 100. The fluid pumped from tank, 104, often contains proppant, which can be sand particles of a particular size. This proppant then flows in the fracture fluid and enters the fractures, 102. The proppant will help maintain fractures open once the pump pressure is removed and when fluids, for example, oil, are produced from the reservoir or fractures. It should be noted that the proppant may move as oil (or another fluid) flows through the fractures.

In figure 1 a controller, 105, is provided which can take measurements from sensors (116 and 115) and/or control valves (108 and 113) and/or actuator (109) and/or pumps (101 and 118) in a prescribed fashion. The applications of this controller will be apparent as various embodiments of this invention are described. It should be noted that the controller can be manually operated but preferably it is automatic. It should also be noted that this same control is preferably used to control the sampling process that will be described later.

In figure 1 a sample tank 106 is shown that will contain the fluid which has the nanoparticles suspended within it. The volume and concentration of the nanoparticles per unit volume are predefined depending on the application. A one-way or non-return valve 107 is provided to allow flow from the sample tank into the flowline 103 but prevents flow back into the tank 106. In some situation it may be necessary to also provide a pump 118 to control the flow of the fluid from the sample tank 106 into the flowline 103. Valve 108 is actuated to open/close by the controller 105. In addition, optionally a flow meter 115 is provided to measure the rate at which the nanoparticle containing fluid enters into the flowline 103. This rate can be controlled to provide a desired nanoparticle concentration per unit volume in the fracturing fluid that is then pumped into the well using pump 101. If the pump 118 is not provided and the nanoparticle fluid is drawn into the flowline 103 then concentration of nanoparticles per unit volume of fracturing fluid is not controlled, however, the rate can be measured by flow meter 115 and recorded by controller 105. It should also be appreciated that in its simplest form this system can be controlled manually so that the valve 108 is open/closed manually by a technician. Therefore, one sample injection embodiment encompasses the components 106, 107, 108 and optionally 115.

Another embodiment also illustrated in figure 1 will now be described. In this embodiment a cylinder, 111, with a plunger, 110, is used to inject the nanoparticle fluid instead of the tank, 106 and pump 118. The plunger is moved by the actuator 109, which is controlled by the controller 105. Initially the plunger is at the top of the cylinder and the fluid containing the nanoparticle is placed in the cylinder, 111, below it. Those skilled in the art will appreciate that the cylinder can be prefilled with nanoparticle laden fluid of a predefined volume and concentration. These samples can be in cartridges (not shown) that are loaded in the cylinder, in a similar manner that caulking is loaded into a caulking gun.

The actuator, 109, is connected to the controller 105. A valve 113 is also connected to the controller and a non-return valve 112 is provided to prevent fluid returning into the cylinder 111. The controller can control the actuator so as to move the plunger, 110, at a given rate in order to inject the sample in the flowline, 103, at a defined flowrate. The controller can use the measured fracturing flowrate from flow meter

116 or from the measured stroke rate of the pump 101 (assuming some efficiency coefficient) to determine the nanoparticle injection rate in order to achieve a certain nanoparticle concentration per unit volume of fracturing fluid. It will be appreciated by those skilled in the art, that certain tracer applications are very long time scale events, for example, months or years in the case of EOR, and nanoparticle injection will need to occur continuously or in slow periodic bursts whose timing is controlled and known. Whereas other applications, for example, tracing for fracturing fluids during a fracturing job, are over much shorter periods and as a result nanoparticles are injected in bursts that can occur over shorter periods. During multistage fracturing jobs where multiple fractures are created along the wellbore, it will be preferable to inject nanoparticles that have different and unique DNA signatures into each fracture stage. This can be achieved by loading different cartridges or nanoparticle fluids into cylinder, 111, after each stage is fractured and before the next one is started. Different DNA signature nanoparticle fluids could equally be placed in sample tank, 106, between fracturing stages. With the controlled application of the systems shown in figure 1, each fracture stage can be traced with unique DNA signature particles and the controlled capture and analysis of these particles once the well starts to flow will allow the quantification of the efficiency of each fracture stage.

In figure 1, it is shown that the two different nanoparticle injection systems; one using the sample tank 106 and the other using the injection cylinder, 111, are repeated as illustrated in the dashed box 117, on the high pressure side of the pump 101. This is to illustrate that these components could be placed downstream of the pump in which case the nanoparticles would not need to pass through the pump. However, the preferred embodiment is as described above where the injection occurs on the low pressure side of the pump 101. In this case, the injection system is exposed to much lower pressures and can be more easily manufactured.

As discussed earlier in this disclosure, during a fracturing operation the fracturing fluid is loaded with proppant. This is often sand of a particular size or size distribution. In another embodiment of this invention, the proppant is used to deliver the nanoparticles into the well and into the fractures. It will be appreciated that other materials that are pumped into a well, for example, gravel used in a gravel pack operation or any other material that is moveable and will be pumped into the well or

fractures, can equally be used to deliver nanoparticles into the flow system. Several embodiments will now be described using figures 2a, 2b and 2c.

In figure 2a a single proppant particle, for example, as sand particle, is shown, 200. Obviously a huge number of such particles will be pumped during a fracturing job. The particle, 200, is coated with a material, 201, that dissolves or degrades in a predefined fashion when it comes into contact with a predefined fluid. For example, the coating, 201, can be manufactured from oil-soluble resins or waxes with tuned melting temperatures or other classes of chemicals that will dissolve in hydrocarbon. The use of oil-soluble resins for example is beneficial because they will not break down under the harsh temperature and pressure environment found in oil wells but will only dissolve/disintegrate when they come into contact with hydrocarbons such as oil. Such coating can be applied via a melt coating process or some other process that is known to those skilled in the art. Those skilled in the art will recognise that other materials could be used that dissolve or breakdown in other fluids such as formation or injected water during an EOR operation. Nanoparticles, 202, are embedded in the coating material, 201 during the manufacturing processes so that the proppant particle 200 is thus coated with a nanoparticle laden material 201. The nanoparticles will in turn encapsulate or have embedded in them DNA of a known and unique signature as disclosed in GB2489714 and PCT/EP2012/056230. In figure 2a, when the fluid, 203, in which the coating, 201, dissolves flows past the proppant particle, the nanoparticles 202 are released and will flow to surface where they are captured and analysed. The proppant particle remains in the well or formation or it may move as a result of the flow 203. The nanoparticles, 202, released are captured at surface as described in other embodiments of this invention. In figure 2b, there is shown schematically proppant particles 200 that are coated in different materials 201 or 203. These coatings have nanoparticles 202 and 204 respectively, embedded within them. In addition, these nanoparticles have different unique DNA signatures. The coatings 201 and 203 will dissolve or degrade in different fluids, for example, 203 could consist of for example, hydrocarbon waxes chosen such that their glass transition temperature is well below the maximum temperature that will be encountered during the process/operation and will dissolve in hydrocarbon and 201 can be made of, for example, polylactic acid or other water soluble polymers such as partially hydrolysed polyacrylamides or polyethylene oxide and will dissolve or

degrade in water. In figure 2b, a first fluid, 205, for example, hydrocarbon flows over the proppant particles and releases the nanoparticles 204 that will flow to surface entrained in the hydrocarbon. At this time the coating 201 remains intact. However, at some later time a different fluid, 206, for example, formation or injected water flows through the proppant particles and dissolves the coating 201 to release nanoparticles 202 which will flow to surface in the water (or likely oil/water mixture) where they can be captured. Those skilled in the art will appreciate that many different coatings 201 or 203 each with its own unique DNA particles can be utilised. For example, different fractures can have particles coated with 201 and/or 203 but with unique DNA nanoparticles that distinguish them from other fractures in the same well. When a particular fluid flows in a particular fracture the nanoparticles released and captured at surface will provide the information to establish exactly what fluid is flowing and from which fracture. In addition, those skilled in the art will appreciate that different coatings can be used that dissolve in fluids of a specific chemical characteristic, for example, fluids of a particular pH or within a particular pH range could cause the coating to dissolve or degrade so as to release the nanoparticles embedded within them. All such combinations are encompassed in this invention. Additionally, for fracturing applications nanoparticles can be encapsulated/embedded in larger capsules whose crush strength is such that they readily break when compressed between the proppant on closure of the fracture (for example the hydrocellulosic materials used to encapsulate gel fluid breakers in fracturing operations). These capsules are placed within the fracture along with the proppant and as the fracture closes, the compressive stresses created cause these materials to rupture and the encapsulated nanoparticles are released at the inception of the clean-up/flow back process. Such particles are captured at surface as described in other elements of this invention and provide more accurate data from the return times of these particles.

Another embodiment is schematically illustrated in figure 2c. In this figure a proppant particle, 200, is first coated with a material 201 that has nanoparticles 202 embedded within it. It is then coated with a second material, 203, that has different and unique other nanoparticles, 204, embedded within it. The nanoparticles 202 and 204 will have different DNA signatures embedded with them making them unique. In figure 2c, a first fluid 205 flows through the proppant, for example, hydrocarbon, which dissolves or degrades the outer coating 203 and thus releases nanoparticles 204. The

capture and analysis of nanoparticles 204 at surface is a unique indication that fluid 205 has flowed past the proppant, 200, wherever it may be initially placed within the well or fracture sequences. At this time, the coating 201 that does not react with fluid 205, remains intact. At some later time, a different fluid 206, for example, formation or injected water, flows through the proppant and dissolves or degrades the coating 201 and so releases the nanoparticles 202 into the water (or oil/water) flow. These particles are returned to surface in this flow where they can be captured and analysed. Those skilled in the art will appreciate that fracturing fluids can be water based and without this double layer system the water soluble coating may be dissolved during the proppant pumping operation, that is, long before the well starts to produce water. This is not desirable and therefore the embodiment disclosed in figure 2c is preferable in such situation, as the inner water-soluble coating, 201, is protected by the outer hydrocarbon-soluble coating, 203. It will be appreciated that other multiple layer configurations can be designed to provide other desired effects such as the dissolution of a coating by simulation fluids such as particular acids. It should also be appreciated that the material used to transport the nanoparticles could be gravel that is commonly used in gravel packing.

Another aspect of this invention is the controlled capture of nanoparticles as they return to surface in the flow from the well. Related embodiments are now described with reference to figures 3, 4 and 5.

Figure 3 shows return flow from fractures 102 generated in the formation as a result of a fracturing operation. The flow returns to surface flowline 303 via the well 100. Optionally, a flowmeter 314 is provided that gives a measure of the rate at which fluid is returning from the well 100. In this disclosure a fracturing operation is used to illustrate the various embodiments of this invention but other operations such as EOR are well known to those skilled in the art and are equally encompassed in this invention. In the case of EOR, the returning flow will be oil and gas swept to the producing well, 100, by water injected in an offset well or wells, not shown. The injected water will have nanoparticles entrained within it that uniquely identify its origin; this will eventually enter the production well, 100, and will subsequently be captured as described herein.

Returning to figure 3, the fluid returning from the well will flow through the flowline 303 into the production return flow system illustrated as tank 304. In the flowline there is provided a nanoparticle detection unit, 301. This unit could have several embodiments. In one embodiment 301 is an inline spectrometer that uses spectral absorption or reflection to identify characteristic signatures that represent the presences of nanoparticles of a particular size within the flow. In another embodiment the nanoparticles are injected in a carrier fluid, for example, a dye or a fluid that fluoresces at a particular wavelength, as explained in other embodiments of this invention, and the detection unit 301 detects the dye or fluorescence by interrogating the fluid as it flows through the unit, for example, by use of electromagnetic waves at a particular wavelength or selection of wavelengths.

In yet another embodiment 301 contains a tab as schematically illustrated in figure 5. In figure 5 the returning flow from the well, 501, contains nanoparticles 502. The nanoparticles, 502, have surface properties to comprise *cis*-diol or alpha-hydroxy acid groups protruding from the outer surface. The collection tab in 301, 503, has a mesh, which is coated with boron acid moiety (for example, phenylboronic acid, benzoboroxole etc). The use of boronic acids for attachment to a diol material or vice versa allows in situ concentration of the particles for ease of sampling and detection. The surface of the collection tab 301, 503, forming a recovery element includes a first chemical moiety adapted to bind chemically to a complementary second chemical moiety located in at least the outer surface of the tracer nanoparticle. The first or second chemical moiety may comprise at least one of a boron acid or a derivative thereof, for example phenylboronic acid or benzoboroxole or a mixture thereof. The first or second chemical moiety may comprise at least one hydroxyl moiety, for example the at least one hydroxyl moiety is present in at least one of a diol or *cis*-diol moiety and an alpha-hydroxy acid moiety or a mixture thereof. The first or second chemical moiety may comprise at least one protein, for example streptavidin, biotin, protein A or any mixture thereof. The first or second chemical moiety may comprise at least one antibody, for example an immunoglobulin G antibody.

These combinations provide a lock and key or donor/receptor type of mechanism. As the functionalised nanoparticles 502 flow over the tab 503, they stick to the tab through the donor/receptor bonds. By this mechanism the nanoparticles are captured

and separated from the returning flow. Another advantage of this embodiment is that it represents a passive capture system that does not require any specific action to retrieve the nanoparticles. In a further embodiment, an electric property of the tab is modified as the number of captured nanoparticles increases. For example, if the tab is initially of low conductance its resistance decreases as the captured nanoparticles provide an increasing current path. Or if the tab comprise multiple layers, the capacitance across these layers changes as the number of nanoparticles captured increases. The change of electric property is measured by means of an appropriated electronic circuit, 505, that is not detailed but is readily appreciated by someone skilled in the art.

In yet another embodiment, the tab can be interrogated by, for example, electromagnetic waves of a given wavelength as illustrated by 506 in figure 5. The resulting reflected or transmitted waves 507 can be used to determine, for example, the degree of fluorescence or colour change of the tab which in turn is an indication of the number of (or change in the number of) nanoparticles stuck to or the loading of nanoparticles on the tab.

The measured change in property or nanoparticle loading is provided to the controller 305 as shown in figures 3 and 4, and the controller can be configured to trigger the action as will be described later with reference to figure 3 or alternatively it could simply inform the operator that nanoparticles have been detected or the tab is now loaded with nanoparticles so it should be removed and replaced as illustrated in figure 4. Once the tab has been removed from 301, it can be treated as disclosed in GB2489714 and PCT/EP2012/056230, to release and break the nanoparticles to release the enclosed DNA for analysis by means known to those skilled in the art, for example, qPCR. Ideally the DNA characterisation and signature matching is achieved using a handheld technology as provided by Bio-Nems, see www.bio-nems.com. Further, providing a means for such a handheld device to take the tab directly, release the nanoparticles, break the nanoparticles to release the DNA and carryout the DNA analysis is preferred.

In another embodiment, the chemical tab described above can be replaced by a magnet, magnetic tab or magnetic separator to capture and detect magnetically-tagged

nanoparticles. This approach uses a physical property rather than a chemical characteristic of the particle to aid detection and measurement and those skilled in the art will appreciate that tags exploiting other physical properties can also be used for this purpose.

In figure 3 the detection of nanoparticles by 301, is used to trigger the collection of a sample or samples. The controller 305 is provided to use such measurements and carryout the required actions. A sampling cylinder 306 is provided to act as a syringe to draw a sample from flowline 303. The controller will open valve 309 and instructing the actuator 308 that is attached to the plunger 307, to draw a sample from the flowline 303 into the cylindrical chamber 306. A non-return valve 310 is provided to prevent flow from returning back into flowline 303. The plunger controller 308 can be actuated on order to take a certain sample volume and at a certain rate. This rate and volume can be controlled using a measure of the flow rate from the well, 314, so as to achieve a certain volume rate per unit volume of flow from the well. Or it could be controlled by the nanoparticle concentration rate as provided by 301 and 314 combined. Once the desired sample is within the chamber 306, the controller 305 can instruct to open a valve 312, in order to allow flow into a sample bottle 313. In figure 3 three sample bottles are shown, however, it will be appreciated that this could be any number and also the bottles could be configured into a carousel (not shown) arrangement so that a given bottles is rotated into position to accept a sample. It is also possible that the cylindrical chamber 306 contains a cartridge that is filled and is removed and replaced with an empty cartridge manually. Once the valve 312 has been opened, the plunger controller 308 is instructed to push the plunger 307 downwards and thus push the sample out of the chamber 306, through the non-return valve 311 and into the selected bottle 313. It will be understood by those skilled in the art that different arrangements of valves and flow networks can be used to achieve that same technical effect and all are encompassed in this invention.

In another embodiment a particle collection tab (chemical or physical/magnetic), as described earlier and schematically shown in figure 5, can be placed inline with a sample bottle as illustrated by 315 in figure 3. By doing this some nanoparticles are captured in the tab 315 that are directly representative of those in the sample collected

in bottle 313 and in some cases can replace the requirement for the sample as the nanoparticles captured on the tab can be readily analysed.

It should be noted that the controller 305 can be the same controller 105, described in other embodiments of this invention as schematically illustrated in figures 1 or the controllers 105 and 305 could be linked in order to share information. As a result, both the nanoparticle injection profiles and the nanoparticle collection profiles can be controlled so that both are by design and in accordance with one another. As an example we consider an EOR operation where water is continually injected into a reservoir in order to sweep oil towards a production well. This water can be injected through a network of wells that surround the production well. This is schematically illustrated in figure 6a where a plan view of a single production well, 600, is shown surrounded by hexagonal array of injection wells 601. Each injection well may be operated independently and water may be continually pumped into it at some predefined rate. As water is injected into all six wells, oil is pushed towards the production well 600 in the centre. Those skilled in the art will be familiar this method of EOR and will also appreciate that the number and location of injection and production wells will vary depending on specific reservoir conditions.

In figure 6b two nanoparticle injection profiles 603 and 606 are shown that may be applied in two different injection wells. The other injection wells may also have nanoparticle injection profiles but these are not shown. In figure 6b, it is assumed that water is being continually injected into a particular well, 601, and the profile 603 represents nanoparticles injected into this injected water as described in other embodiments of this invention. The nanoparticle injection profile is controlled by the controller 105, and a pulse of nanoparticles with a concentration and duration represented by the height and width of 604, respectively, is injected into the injected water. The nanoparticle pulses are repeated at a regular interval of 605. As an example, a pulse of 6 hours duration could be repeated every 10 days. EOR operations are generally very long term operations that can continue for years so the interval between nanoparticle pulses could be weeks or even months. Each pulse of nanoparticles 604 will contain DNA signatures that are unique and different thus uniquely identifying each and every pulse. In figure 6b a second nanoparticle injection profile, 606, is shown to illustrate that profiles of different concentration,

duration and/or interval may be applied to a different injection well, 602, and the other injection wells may have other different profiles that are not shown. In addition, each nanoparticle injection pulse can comprise a 'carrier' fluid that is readily detected as described in other embodiments. The same carrier fluid, e.g., a particular dye, can be used in all injection wells because the unique 'signal' identifying the origin and injection time etc., is contained within the DNA that is embedded within the nanoparticles. The carrier simply provides an indication to the sampling system that a sample (or samples) should be taken as describe in other embodiments. In other embodiments a nanoparticle capture tab could also be used to the same effect.

The nanoparticle pulses injected into the injection wells 601 will pass through the reservoir with the injected water, pushing oil towards the production well 600. Eventually they may enter the well 600 and will flow to surface. The sampling systems as described elsewhere will capture the nanoparticles as they are carried with the injected water. Figure 6c shows a schematic illustration of a nanoparticle pulse profile, 607, captured in the flow from the production well 600. The DNA signature within the nanoparticles can be used to identify from which injection well the nanoparticles came and indeed can indicate the exact nanoparticle injection pulse. Therefore, the injection profile, for example, 603, can be compared to the capture profile 607. As a result of this comparison, important information relating to the flow of fluid through the reservoir between wells 601 and 600, in this case, can be determined. For example, the time between the pulses 604 and 608 will provide the transit time for the fluid through the reservoir. The width of pulse 608 as compared to 604 can be related to the dispersion within the reservoir. Such comparisons contain important information about a number of reservoir characteristics such as permeability, relative permeability, absorption behaviour, distribution of fluid flow paths etc. The change in pulse interval 605 to 609 can provide information related to the change in transit time as the flow changes from mostly oil to mostly water. This is because ahead of pulse 608 it is oil that is primarily flowing but between 608 and 610 the amount of water is increasing. Samples taken during pulse 608, 610 and future pulses can be analysed to determine changes in the oil/water ratio and this change can be determined with time and provide important information about relative permeability characteristics. In another embodiment of this this invention, the injection controller 105 can be instructed to change, for example, the nanoparticle

pulse interval period into well 601 as a result of information obtained from the capture profile 607. For example, it may be advantageous to increase the nanoparticle pulse concentration and/or duration and/or reduce the interval period in order to increase the resolution of reservoir transit calculations. These calculations can be used to calibrate the reservoir model used to control the EOR operation. As a result, water injection rates into the wells 601 may be adjusted to improve the overall oil sweep efficiency. This information can also be used to trigger or define the sampling characteristics, for example, the sampling frequency or duration. This granularity of reservoir calibrations is not possible with the technology available today but is possible through the embodiments described herein because of the flexibility of control of both the nanoparticle tracer injection and capture systems.

In this detailed description several embodiments of this invention are described. They provide a detailed description of the concepts captured in this invention. However, it is by no means exhaustive and those skilled in the art will appreciate that other embodiments are possible which use the concepts described. These other potential embodiments cannot all be described but are however encompassed within the scope of this invention.

Claims:

1. A tracer particle for use in the exploration, production, transportation and/or storage of oil and/or gas, the tracer particle comprising a proppant material, a coating layer at least partially surrounding the proppant material and a tracer material within the coating layer, the tracer material having an identifiable DNA.
2. A tracer particle according to claim 1 wherein the proppant material comprises sand particles, gravel particles, synthetic ceramic materials, or any mixture thereof.
3. A tracer particle according to claim 1 or claim 2 wherein the tracer material comprises a plurality of nanoparticles having identifiable DNA dispersed within the coating layer.
4. A tracer particle according to any one of claims 1 to 3 wherein an outer surface of at least some of the nanoparticles is functionalised for capture by a physical or chemical mechanism.
5. A tracer particle according to claim 4 wherein the outer surface of at least some of the nanoparticles is chemically functionalised for capture by a chemical mechanism.
6. A tracer particle according to claim 5 wherein the outer surface of at least some of the nanoparticles comprises at least one protein, at least one antibody, and/or at least one hydroxyl moiety, located in at least an outer surface of the coating layer.
7. A tracer particle according to claim 6 wherein the at least one protein comprises streptavidin, biotin, protein A or any mixture thereof, the at least one antibody comprises an immunoglobulin G antibody, and/or the at least one hydroxyl moiety is present in at least one of a diol or *cis*-diol moiety and an alpha-hydroxy acid moiety or a mixture thereof.
8. A tracer particle according to any one of claims 1 to 7 wherein the identifiable DNA is complexed with a complexing agent.
9. A tracer particle according to claim 8 wherein the complexing agent is a complexing polymer.
10. A tracer particle according to any one of claims 1 to 9 wherein the identifiable DNA is at least partly encapsulated by an encapsulating polymer.

11. A tracer particle according to claim 10 wherein the encapsulating polymer comprises at least one acrylate-, methacrylate- or styrene-based polymer.
12. A tracer particle according to claim 11 wherein the encapsulating polymer is a cross-linked polymer including a cross-linker.
13. A tracer particle according to claim 12 wherein the cross-linker is adapted to be chemically reduced by a reducing agent thereby to degrade the encapsulating polymer to release the DNA for analysis, optionally a disulfide cross-linker.
14. A tracer particle according to any one of claims 1 to 13 wherein the coating layer comprises an oil-soluble or water-soluble material.
15. A tracer particle according to claim 14 wherein the oil-soluble material is selected from a hydrocarbon wax, a resin, a polymer or any mixture of two or more thereof.
16. A tracer particle according to claim 15 wherein the water-soluble material is at least one polymer.
17. A tracer particle according to claim 16 wherein the at least one polymer comprises polylactic acid, partially hydrolysed polyacrylamide, polyethylene oxide or any mixture of two or more thereof.
18. A tracer sample comprising a plurality of tracer particles according to any one of claims 1 to 17, the tracer particles comprising a mixture of a plurality of first tracer particles and a plurality of second tracer particles, the first tracer particles comprising a first tracer material and the second tracer particles comprising a second tracer material, wherein the first and second tracer materials have different identifiable DNA, and the coating layers of the first and second tracer particles comprise respective first and second oil-soluble and/or water-soluble material which have respective different solubility in oil and/or water.
19. A tracer sample according to claim 18 wherein the coating layer of the first tracer particles comprises an oil-soluble material and the coating layer of the second tracer particles comprises a water-soluble material.
20. A tracer particle according to any one of claims 1 to 13 wherein the coating layer is an inner coating layer with a first tracer material therein, and the tracer particle further comprises an outer coating layer at least partially surrounding the inner coating layer and a second tracer material within the outer coating

layer, wherein the first and second tracer materials have different identifiable DNA and the inner and outer coating layers comprise respective first and second oil-soluble and/or water-soluble material which have respective different solubility in oil and/or water.

21. A tracer particle according to claim 20 wherein the outer coating layer comprises an oil-soluble material and the inner coating layer comprises a water-soluble material.
22. A tracer particle according to claim 20 or claim 21 wherein the oil-soluble material is selected from a hydrocarbon wax, a resin, a polymer or any mixture of two or more thereof.
23. A tracer particle according to any one of claims 20 to 22 wherein the water-soluble material is at least one polymer.
24. A tracer particle according to claim 23 wherein the at least one polymer comprises polylactic acid, partially hydrolysed polyacrylamide, polyethylene oxide or any mixture of two or more thereof.
25. A tracer particle in the form of a capsule comprising an outer shell encapsulating tracer material which comprises a plurality of nanoparticles having identifiable DNA.
26. A tracer particle according to claim 25 wherein an outer surface of at least some of the nanoparticles is functionalised for capture by a physical or chemical mechanism.
27. A tracer particle according to claim 26 wherein the outer surface of at least some of the nanoparticles is chemically functionalised for capture by a chemical mechanism.
28. A tracer particle according to claim 27 wherein the outer surface of at least some of the nanoparticles comprises at least one protein, at least one antibody, and/or at least one hydroxyl moiety, located in at least an outer surface of the coating layer.
29. A tracer particle according to claim 28 wherein the at least one protein comprises streptavidin, biotin, protein A or any mixture thereof, the at least one antibody comprises an immunoglobulin G antibody, and/or the at least one hydroxyl moiety is present in at least one of a diol or *cis*-diol moiety and an alpha-hydroxy acid moiety or a mixture thereof.

30. A tracer particle according to any one of claims 25 to 29 wherein the identifiable DNA is complexed with a complexing agent.
31. A tracer particle according to claim 30 wherein the complexing agent is a complexing polymer.
32. A tracer particle according to any one of claims 25 to 31 wherein the identifiable DNA is at least partly encapsulated by an encapsulating polymer.
33. A tracer particle according to claim 32 wherein the encapsulating polymer comprises at least one acrylate-, methacrylate- or styrene-based polymer.
34. A tracer particle according to claim 33 wherein the encapsulating polymer is a cross-linked polymer including a cross-linker.
35. A tracer particle according to claim 34 wherein the cross-linker is adapted to be chemically reduced by a reducing agent thereby to degrade the encapsulating polymer to release the DNA for analysis, optionally a disulfide cross-linker.
36. A tracer particle according to any one of claims 25 to 35 wherein the outer shell comprises at least one cellulose material, optionally hydrocellulose.
37. A plurality of tracer particles according to any one of claims 1 to 17 or 20 to 36 or a tracer sample according to claim 18 or claim 19 wherein the tracer particles are present in a carrier fluid which comprises a detectable indicator in addition to the tracer material.
38. A plurality of tracer particles or a tracer sample according to claim 37 wherein the detectable indicator comprises at least one dye.
39. A method of tracing fluid during the exploration, production and/or storage of oil and/or gas, the method comprising the steps of:
 - (i) providing a tracer particle comprising (a) a proppant material, a coating layer at least partially surrounding the proppant material and a tracer material within the coating layer, the tracer material having an identifiable DNA or (b) a capsule comprising an outer shell encapsulating tracer material which comprises a plurality of nanoparticles having identifiable DNA;
 - (ii) introducing the tracer particle into a fluid;
 - (iii) injecting the fluid, containing the tracer particle therein, into a supply of oil or gas;

- (iv) subsequently recovering at least some of the tracer material which was in the injected fluid; and
 - (v) analyzing any identifiable DNA in the tracer material.
40. A method according to claim 39 wherein in step (iii) the fluid is injected, either as a pulse or continuously, into a flow of a second fluid which may or may not contain a proppant.
41. A method according to claim 40 wherein in step (iii) the fluid is injected as a sequence of intermittent pulses.
42. A method according to claim 40 or claim 41 wherein a plurality of the oil or gas wells is provided, and in step (iii) a respective sample of the fluid is injected as a respective pulse into a respective well or at least two of the respective wells, and optionally in preceding or subsequent injection operations a pulse of a further tracer material comprising a plurality of nanoparticles having an identifiable DNA and in the absence of proppant material is injected into the respective well or at least two of the respective wells.
43. A method according to claim 42 wherein in step (iii) the fluid is injected sequentially into the at least two of the respective wells.
44. A method according to any one of claims 39 to 43 wherein in step (iii) an injection time that the fluid is injected is recorded and in step (iv) a recovery time that the tracer material is recovered is recorded.
45. A method according to claim 44 wherein a residence time between the injection and recovery times is determined.
46. A method according to claim 45 wherein the residence time is input as a parameter into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.
47. A method according to claim 46 wherein the parameter is adapted to function as a calibration parameter for the computer model.
48. A method according to any one of claims 39 to 47 wherein in step (iii) an injection time period during which the fluid is injected is recorded and in step (iv) a recovery time period during which the tracer material is recovered is recorded.
49. A method according to claim 48 wherein a time period relationship between the injection time period and the recovery time period is determined.

50. A method according to claim 49 wherein a variation of the time period relationship with time is determined.
51. A method according to claim 49 or claim 50 wherein at least one of the time period relationship or the variation of the time period relationship with time is input as a parameter, optionally as a calibration parameter, into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.
52. A method according to any one of claims 39 to 51 wherein in step (iii) in a first injection operation a first tracer material is injected and subsequently in a second injection operation a second tracer material, optionally in the presence or absence of proppant material, is injected, the first and second tracer materials having different identifiable DNA.
53. A method according to any one of claims 39 to 52 wherein in step (iii) the injected fluid comprises a known initial concentration of the tracer material and in step (iv) a final concentration of the recovered tracer material is recorded.
54. A method according to claim 53 wherein in step (iii) the known initial concentration of the tracer material varies with time and in step (iv) a final concentration, varying with time, of the recovered tracer material is recorded.
55. A method according to claim 53 or claim 54 wherein a concentration relationship between the initial and final concentrations is determined.
56. A method according to claim 55 wherein a variation of the concentration relationship with time is determined.
57. A method according to claim 55 or claim 56 wherein at least one of the concentration relationship or the variation of the concentration relationship with time is input as a parameter into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.
58. A method according to any one of claims 39 to 57 wherein in step (iii) the fluid comprises a detectable indicator in addition to the tracer material.
59. A method according to claim 58 wherein the detectable indicator comprises at least one dye.
60. A method according to any one of claims 39 to 59 wherein in step (iii) the fluid is injected into an oil or gas well in a hydraulic fracturing operation.

61. A method according to claim 60 wherein during the hydraulic fracturing operation the coating layer is degraded within the well to release the tracer material into the well.
62. A method according to any one of claims 39 to 61 further comprising the step of injecting into the respective well or at least two of the respective wells a pulse of a further tracer material comprising a plurality of nanoparticles having an identifiable DNA and in the absence of proppant material in an enhanced oil recover (EOR) operation.
63. A method according to claim 62 wherein a plurality of the oil or gas wells is provided defining a central area therebetween, and in step (iii) a respective sample of the fluid is injected into a respective well or at least two of the respective wells, each sample having a respective tracer material therein.
64. A method according to any one of claims 39 to 63 wherein in step (ii) the tracer particle is introduced into the fluid after the fluid has been pressurized to an injection pressure.
65. A method according to claim 64 wherein in step (ii) the injection pressure is controlled or varied to control or vary the injection rate in step (iii).
66. A method according to any one of claims 39 to 65 wherein in step (ii) a plurality of the tracer particles are introduced into the fluid at a known concentration and/or at a known dosage rate and/or over a known time period.
67. A method according to any one of claims 39 to 66 wherein the supply of oil or gas is monitored to detect the fluid, any nanoparticles having an identifiable DNA therein or any identifiable DNA therein, and step (iv) is initiated after detection of the fluid or any nanoparticles having the identifiable DNA or any identifiable DNA in the supply of oil or gas.
68. A method according to claim 67 wherein the monitoring of the supply of oil or gas includes measuring a physical property of the fluid or any tracer material therein, the physical property being selected from absorption and/or reflection and/or scattering of electromagnetic radiation, dielectric constant, colour in the visible region of the spectrum, and fluorescence, or any combination thereof.
69. A method according to any one of claims 39 to 68 wherein in step (iv) the tracer material is captured on a surface of a recovery element, the surface being adapted to bind chemically or physically to a surface of the tracer material.

70. A method according to claim 69 wherein the tracer material comprises a plurality of nanoparticles having identifiable DNA.
71. A method according to claim 70 wherein the surface of the recovery element includes a first chemical moiety adapted to bind chemically to a complementary second chemical moiety on the surface of the tracer nanoparticle.
72. A method according to claim 71 wherein the first or second chemical moiety comprises at least one of a boron acid or a derivative thereof.
73. A method according to claim 72 wherein the first or second chemical moiety comprises phenylboronic acid or benzoboroxole or a mixture thereof.
74. A method according to any one of claims 71 to 73 wherein the first or second chemical moiety comprises at least one hydroxyl moiety.
75. A method according to claim 74 wherein the at least one hydroxyl moiety is present in at least one of a diol or *cis*-diol moiety and an alpha-hydroxy acid moiety or a mixture thereof.
76. A method according to claim 75 wherein the first or second chemical moiety comprises at least one protein.
77. A method according to claim 76 wherein the at least one protein comprises streptavidin, biotin, protein A or any mixture thereof.
78. A method according to claim 76 or claim 77 wherein the first or second chemical moiety comprises at least one antibody.
79. A method according to claim 78 wherein the at least one antibody comprises an immunoglobulin G antibody.
80. A method according to any one of claims 70 to 79 wherein the surface of the recovery element is monitored to indicate, directly or indirectly, capture of the nanoparticle on the surface of the recovery element.
81. A method according to claim 80 wherein the electrical properties or visual appearance of the surface of the recovery element is monitored.
82. A method according to claim 80 or claim 81 wherein the surface of the recovery element is monitored to indicate, directly or indirectly, an amount of the nanoparticle captured on the surface of the recovery element.
83. A method according to claim 82 wherein the indicated amount of the nanoparticle captured on the surface of the recovery element reaches a

- predetermined threshold, the analysis step (v) is initiated for the nanoparticle captured on the surface of the recovery element.
84. A method according to any one of claims 39 to 83 wherein in step (iii) a predetermined volume of the fluid, having a predetermined concentration of the identifiable DNA, is injected.
85. A method according to claim 84 wherein in step (iii) the predetermined volume of the fluid is injected from a cartridge containing the predetermined volume.
86. A method according to claim 84 wherein in step (iii) the predetermined volume of the fluid is injected by a plunger mechanism.
87. A method according to claim 84 wherein in step (iii) the predetermined volume of the fluid is injected from a tank through a flowmeter.
88. A method according to any one of claims 39 to 87 wherein the proppant material comprises sand particles, gravel particles, synthetic ceramic materials or any mixture thereof.
89. A method according to any one of claims 39 to 88 wherein the tracer material comprises a plurality of nanoparticles having identifiable DNA dispersed within the coating layer.
90. A method according to claim 89 wherein an outer surface of at least some of the nanoparticles is functionalised for capture by a physical or chemical mechanism.
91. A method according to claim 90 wherein the outer surface of at least some of the nanoparticles is chemically functionalised for capture by a chemical mechanism.
92. A method according to claim 91 wherein the outer surface of at least some of the nanoparticles comprises at least one protein, at least one antibody, and/or at least one hydroxyl moiety, located in at least an outer surface of the nanoparticle.
93. A method according to claim 92 wherein the at least one protein comprises streptavidin, biotin, protein A or any mixture thereof, the at least one antibody comprises an immunoglobulin G antibody, and/or the at least one hydroxyl moiety is present in at least one of a diol or *cis*-diol moiety and an alpha-hydroxy acid moiety or a mixture thereof.

94. A method according to any one of claims 39 to 93 wherein the coating layer comprises an oil-soluble or water-soluble material.
95. A method according to claim 94 wherein the oil-soluble material is selected from a hydrocarbon wax, a resin, a polymer or any mixture of two or more thereof.
96. A method according to claim 94 or claim 95 wherein the oil-soluble material at least partly dissolves in at least one hydrocarbon present in the oil or gas well.
97. A method according to claim 96 wherein the water-soluble material is at least one polymer.
98. A method according to claim 97 wherein the at least one polymer comprises polylactic acid, partially hydrolysed polyacrylamide, polyethylene oxide or any mixture of two or more thereof.
99. A method according to any one of claims 94 to 98 wherein the water-soluble material at least partly dissolves in at least one aqueous liquid present in the oil or gas well.
100. A method according to any one of claims 39 to 99, wherein in step (iii) a plurality of tracer particles is injected, the tracer particles comprising a mixture of a plurality of first tracer particles and a plurality of second tracer particles, the first tracer particles comprising a first tracer material and the second tracer particles comprising a second tracer material, wherein the first and second tracer materials have different identifiable DNA, and the coating layers of the first and second tracer particles comprise respective first and second oil-soluble and/or water-soluble material which have respective different solubility in oil and/or water.
101. A method according to claim 100 wherein the coating layer of the first tracer particles comprises an oil-soluble material and the coating layer of the second tracer particles comprises a water-soluble material.
102. A method according to any one of claims 39 to 101 wherein the coating layer is an inner coating layer with a first tracer material therein, and the tracer particle further comprises an outer coating layer at least partially surrounding the inner coating layer and a second tracer material within the outer coating layer, wherein the first and second tracer materials have different identifiable DNA and the inner and outer coating layers comprise respective

first and second oil-soluble and/or water-soluble material which have respective different solubility in oil and/or water.

103. A method according to claim 102 wherein the outer coating layer comprises an oil-soluble material and the inner coating layer comprises a water-soluble material.
104. A method according to claim 102 or claim 103 wherein the oil-soluble material is selected from a hydrocarbon wax, a resin, a polymer or any mixture of two or more thereof.
105. A method according to any one of claims 102 to 104 wherein the water-soluble material is at least one polymer.
106. A method according to claim 105 wherein the at least one polymer comprises polylactic acid, partially hydrolysed polyacrylamide, polyethylene oxide or any mixture of two or more thereof.
107. A method any one of claims 39 to 106 wherein the outer shell comprises a cellulose material, optionally hydrocellulose.
108. A method according to any one of claims 39 to 107 wherein the outer shell fractures under compression within an oil or gas well to release the nanoparticles encapsulated therein into the oil or gas well.
109. An apparatus for tracing fluid during the exploration, production, transportation and/or storage of oil and/or gas, the apparatus comprising an injector unit for injecting a pulse of fluid, containing at least one tracer particle, including tracer material having identifiable DNA, therein, into a supply of oil or gas; a monitoring unit for monitoring the supply of oil or gas to detect the fluid or any tracer material therein; a recovery unit for subsequently recovering at least some of the tracer material which was in the injected fluid, the recovery unit includes a recovery element having a surface adapted to bind chemically or physically to a surface of the tracer material to capture the tracer material on the recovery element; an analysis unit for analyzing any identifiable DNA in the tracer material, and a controller for controlling the operation of at least one of the injector unit, the monitoring unit, the recovery unit and the analysis unit or any combination thereof.
110. An apparatus according to claim 109 wherein the injector unit is adapted to inject the fluid as a sequence of intermittent pulses.

111. An apparatus according claim 109 or claim 110 wherein the controller is adapted to record an injection time that the fluid is injected by the injector unit and a recovery time that the tracer material is recovered by the recovery unit.
112. An apparatus according claim 111 wherein the controller is adapted to determine a residence time between the injection and recovery times.
113. An apparatus according claim 112 wherein the controller is adapted to input the residence time as a parameter, optionally a calibration parameter into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.
114. An apparatus according any one of claims 109 to 113 wherein the controller is adapted to record an injection time period during which the fluid is injected by the injector unit and a recovery time period during which the tracer material is recovered by the recovery unit.
115. An apparatus according to claim 114 wherein the controller is adapted to determine a time period relationship between the injection time period and the recovery time period.
116. An apparatus according to claim 115 wherein the controller is adapted to determine a variation of the time period relationship with time.
117. An apparatus according to claim 115 or claim 116 wherein the controller is adapted to input at least one of the time period relationship or the variation of the time period relationship with time as a parameter, optionally a calibration parameter, into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.
118. An apparatus according any one of claims 109 to 117 wherein the controller is adapted to record a concentration of the tracer material injected by the injector unit and/or recovered by the recovery unit.
119. An apparatus according to claim 118 wherein the controller is adapted to determine a concentration relationship between the concentration of the tracer material injected by the injector unit and the concentration of the tracer material recovered by the recovery unit.
120. An apparatus according to claim 119 wherein the controller is adapted to determine a variation of the concentration relationship with time.

121. An apparatus according to claim 119 or claim 120 wherein the controller is adapted to input at least one of the concentration relationship or the variation of the concentration relationship with time as a parameter, optionally a calibration parameter, into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.
122. An apparatus according any one of claims 109 to 121 wherein the monitoring unit includes a measuring device for measuring a physical property of the fluid or any tracer material therein, the physical property being selected from absorption and/or reflection and/or scattering of electromagnetic radiation, dielectric constant, colour in the visible region of the spectrum, and fluorescence, or any combination thereof.
123. An apparatus according any one of claims 109 to 122 wherein the surface of the recovery element includes a first chemical moiety adapted to bind chemically to a complementary second chemical moiety on the surface of the tracer material.
124. An apparatus according to claim 123 wherein the first chemical moiety comprises at least one of a boron acid or a derivative thereof.
125. An apparatus according to claim 123 wherein the first chemical moiety comprises phenylboronic acid or benzoboroxole or a mixture thereof.
126. An apparatus according to claim 123 wherein the first chemical moiety comprises at least one protein.
127. An apparatus according to claim 126 wherein the at least one protein comprises streptavidin, biotin, protein A or any mixture thereof.
128. An apparatus according to claim 123 wherein the first chemical moiety comprises at least one antibody.
129. A method according to claim 128 wherein the at least one antibody comprises an immunoglobulin G antibody.
130. An apparatus according to any one of claims 109 to 129 wherein the monitoring unit is adapted to monitor the surface of the recovery element to indicate, directly or indirectly, capture of the tracer material on the surface of the recovery element.

131. An apparatus according to claim 130 wherein the monitoring unit is adapted to monitor electrical properties or visual appearance of the surface of the recovery element.
132. An apparatus according to claim 130 or claim 131 wherein the monitoring unit is adapted to monitor the surface of the recovery element to indicate, directly or indirectly, an amount of the tracer material captured on the surface of the recovery element.
133. An apparatus according to claim 132 wherein the controller is adapted to initiate the analysis unit to analyse the tracer material captured on the surface of the recovery element after an indicated amount of the tracer material captured on the surface of the recovery element reaches a predetermined threshold.
134. An apparatus according to any one of claims 109 to 133 wherein the injector unit is adapted to inject a predetermined volume of the fluid is injected.
135. An apparatus according to claim 134 wherein the injector unit is adapted to inject the predetermined volume of the fluid from a cartridge containing the predetermined volume.
136. An apparatus according to claim 135 wherein the injector unit is adapted to inject the predetermined volume of the fluid by a plunger mechanism.
137. An apparatus according to claim 136 wherein the injector unit is adapted to inject the predetermined volume of the fluid from a tank through a flowmeter.
138. A tracer nanoparticle for use in the exploration, production, transportation and/or storage of oil and/or gas, the tracer nanoparticle comprising a tracer material having an identifiable DNA, and at least one chemical moiety located in at least an outer surface of the tracer nanoparticle, the at least one chemical moiety comprising at least one protein, at least one antibody, and/or at least one hydroxyl moiety.
139. A tracer nanoparticle according to claim 138 wherein the at least one protein comprises streptavidin, biotin, protein A or any mixture thereof.
140. A tracer nanoparticle according to claim 138 wherein the at least one antibody comprises an immunoglobulin G antibody.

141. A tracer nanoparticle according to claim 138 wherein the at least one hydroxyl moiety is present in at least one of a diol or *cis*-diol moiety and an alpha-hydroxy acid moiety or a mixture thereof.
142. A tracer nanoparticle according to any one of claims 138 to claim 141 wherein the identifiable DNA is complexed with a complexing agent, optionally wherein the complexing agent is a complexing polymer.
143. A tracer nanoparticle according to any one of claims 138 to 142 wherein the identifiable DNA is at least partly encapsulated by an encapsulating polymer, optionally wherein the encapsulating polymer comprises at least one acrylate-, methacrylate- or styrene-based polymer, further optionally wherein the encapsulating polymer is a cross-linked polymer including a cross-linker, yet further optionally wherein the cross-linker is adapted to be chemically reduced by a reducing agent thereby to degrade the encapsulating polymer to release the DNA for analysis, optionally a disulfide cross-linker.
144. A tracer particle having an outer surface which is provided by a coating layer of an oil-soluble or water-soluble material which encapsulates a plurality of the nanoparticles according to any one of claims 138 to 143.
145. A tracer particle according to claim 144 further comprising a proppant material at least partly surrounded by the coating layer, optionally wherein the proppant material comprises a sand particle, a gravel particle, a synthetic ceramic material, or any mixture thereof.
146. A tracer sample comprising a plurality of tracer particles according to claim 144 or claim 145, the tracer particles comprising a mixture of a plurality of first tracer particles and a plurality of second tracer particles, the first tracer particles comprising a first tracer material and the second tracer particles comprising a second tracer material, wherein the first and second tracer materials have different identifiable DNA, and the coating layers of the first and second tracer particles comprise respective first and second oil-soluble and/or water-soluble material which have respective different solubility in oil and/or water.
147. A tracer sample according to claim 146 wherein the coating layer of the first tracer particles comprises an oil-soluble material and the coating layer of the second tracer particles comprises a water-soluble material.

148. A tracer particle according to claim 144 or claim 145 wherein the coating layer is an inner coating layer with a first tracer material therein, and the tracer particle further comprises an outer coating layer at least partially surrounding the inner coating layer and a second tracer material within the outer coating layer, wherein the first and second tracer materials have different identifiable DNA and the inner and outer coating layers comprise respective first and second oil-soluble and/or water-soluble material which have respective different solubility in oil and/or water.
149. A tracer particle according to claim 148 wherein the outer coating layer comprises an oil-soluble material and the inner coating layer comprises a water-soluble material.
150. A tracer particle according to any one of claims 144 to 149 wherein the oil-soluble material is selected from a hydrocarbon wax, a resin, a polymer or any mixture of two or more thereof.
151. A tracer particle according to any one of claims 144 to 150 wherein the water-soluble material is at least one polymer.
152. A tracer particle according to claim 151 wherein the at least one polymer comprises polylactic acid, partially hydrolysed polyacrylamide, polyethylene oxide or any mixture of two or more thereof.
153. A method of tracing fluid during the exploration, production, transportation and/or storage of oil and/or gas, the method comprising the steps of:
- (i) providing tracer nanoparticles comprising a tracer material having an identifiable DNA, and at least one chemical moiety located in at least an outer surface of the tracer nanoparticles;
 - (ii) introducing the tracer nanoparticles into a fluid;
 - (iii) injecting the fluid, containing the tracer nanoparticles therein, into a supply of oil or gas;
 - (iv) subsequently recovering at least some of the tracer material which was in the injected fluid, wherein in step (iv) the tracer material is captured on a surface of a recovery element, the surface being adapted to bind chemically or physically to the at least one chemical moiety; and
 - (v) analyzing any identifiable DNA in the tracer material.

154. A method according to claim 153 wherein the surface of the recovery element includes a first chemical moiety adapted to bind chemically to a complementary second chemical moiety located in at least the outer surface of the tracer nanoparticle.
155. A method according to claim 154 wherein the first or second chemical moiety comprises at least one of a boron acid or a derivative thereof.
156. A method according to claim 155 wherein the first or second chemical moiety comprises phenylboronic acid or benzoboroxole or a mixture thereof.
157. A method according to any one of claims 154 to 156 wherein the first or second chemical moiety comprises at least one hydroxyl moiety.
158. A method according to claim 157 wherein the at least one hydroxyl moiety is present in at least one of a diol or *cis*-diol moiety and an alpha-hydroxy acid moiety or a mixture thereof.
159. A method according to claim 154 wherein the first or second chemical moiety comprises at least one protein.
160. A method according to claim 159 wherein the at least one protein comprises streptavidin, biotin, protein A or any mixture thereof.
161. A method according to claim 159 or claim 160 wherein the first or second chemical moiety comprises at least one antibody.
162. A method according to claim 161 wherein the at least one antibody comprises an immunoglobulin G antibody.
163. A method according to any one of claims 153 to 162 wherein the surface of the recovery element is monitored to indicate, directly or indirectly, capture of the tracer nanoparticle on the surface of the recovery element.
164. A method according to claim 163 wherein the electrical properties or visual appearance of the surface of the recovery element is monitored.
165. A method according to claim 163 or claim 164 wherein the surface of the recovery element is monitored to indicate, directly or indirectly, an amount of the tracer nanoparticles captured on the surface of the recovery element.
166. A method according to claim 165 wherein when the indicated amount of the tracer nanoparticles captured on the surface of the recovery element reaches a predetermined threshold, the analysis step (v) is initiated for the tracer nanoparticles captured on the surface of the recovery element.

167. A method of tracing fluid during the exploration or production of oil and/or gas, the method comprising the steps of:
- (i) providing a tracer particle comprising a tracer material, the tracer material having an identifiable DNA;
 - (ii) introducing the tracer particle into a fluid;
 - (iii) injecting the fluid, containing the tracer particle therein, into a supply of oil or gas, and recording an injection parameter;
 - (iv) subsequently recovering at least some of the tracer material which was in the injected fluid, and recording a recovery parameter;
 - (v) analyzing any identifiable DNA in the tracer material; and
 - (vi) before, simultaneously with, or after step (v), comparing the injection and recovery parameters to determine a property of the oil or gas reservoir and/or well and/or a property of the behaviour of the tracer particle or tracer material within the oil or gas reservoir and/or well.
168. A method according to claim 167 wherein in step (iii) the injection parameter has a first variable and in step (iv) the recovery parameter has a second variable, and in step (vi) the first and second variables are compared.
169. A method according to claim 167 or claim 168 wherein in step (iii) the fluid is injected as a pulse.
170. A method according to claim 167 or claim 168 wherein in step (iii) the fluid is injected as a sequence of intermittent pulses.
171. A method according claim 169 or claim 170 wherein a plurality of the oil or gas wells is provided, and in step (iii) a respective sample of the fluid is injected as a respective pulse into a respective well of at least two of the respective wells.
172. A method according to claim 171 wherein in step (iii) the fluid is injected sequentially into the at least two of the respective wells.
173. A method according to any one of claims 167 to 171 wherein in step (iii) an injection time that the fluid is injected is recorded and in step (iv) a recovery time that the tracer material is recovered is recorded.
174. A method according to claim 173 wherein a residence time between the injection and recovery times is determined.
175. A method according to claim 174 wherein the residence time is input as a parameter, optionally a calibration parameter, into a computer model of a

production system including one or more oil or gas reservoirs or wells or any combination thereof.

176. A method according to any one of claims 167 to 175 wherein in step (iii) an injection time period during which the fluid is injected is recorded and in step (iv) a recovery time period during which the tracer material is recovered is recorded.

177. A method according to claim 176 wherein a time period relationship between the injection time period and the recovery time period is determined.

178. A method according to claim 177 wherein a variation of the time period relationship with time is determined.

179. A method according to claim 177 or claim 178 wherein at least one of the time period relationship or the variation of the time period relationship with time is input as a parameter into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.

180. A method according to any one of claims 167 to 179 wherein in step (iii) in a first injection operation a first tracer material is injected and subsequently in a second injection operation a second tracer material is injected, the first and second tracer materials having different identifiable DNA.

181. A method according to any one of claims 167 to 180 wherein in step (iii) the injected fluid comprises a known initial concentration of the tracer material and in step (iv) a final concentration of the recovered tracer material is recorded.

182. A method according to claim 181 wherein in step (iii) the known initial concentration of the tracer material varies with time and in step (iv) a final concentration, varying with time, of the recovered tracer material is recorded.

183. A method according to claim 181 or claim 182 wherein a concentration relationship between the initial and final concentrations is determined.

184. A method according to claim 183 wherein a variation of the concentration relationship with time is determined.

185. A method according to claim 183 or claim 184 wherein at least one of the concentration relationship or the variation of the concentration relationship with time is input as a parameter, optionally a calibration parameter, into a

computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.

186. A method of tracing fluid during the exploration and/or production, of oil and/or gas, the method comprising the steps of:

- (i) providing a tracer particle encapsulating a tracer material, the tracer material having an identifiable DNA;
- (ii) introducing the tracer particle into a fluid;
- (iii) injecting the fluid, containing the tracer particle therein, into an oil or gas well in a hydraulic fracturing operation;
- (iv) releasing the encapsulated tracer material having identifiable DNA, by compression of the tracer particle, or at least partial dissolution of encapsulant encapsulating the tracer material, in a fracture within the oil or gas well;
- (v) subsequently recovering at least some of the tracer material which was in the injected fluid;
- (vii) analyzing any identifiable DNA in the tracer material; and
- (viii) before, simultaneously with, or after step (v), determining the fracture closure time by analysis of the period between the injection time in step (iii) and the recovery time in step (v).

187. A method according to claim 186 wherein in step (iii) the fluid is injected as a pulse.

188. A method according to claim 187 wherein in step (iii) the fluid is injected as a sequence of intermittent pulses.

189. A method according to claim 187 or claim 188 wherein a plurality of the oil or gas wells is provided, and in step (iii) a respective sample of the fluid is injected as a respective pulse into a respective well of at least two of the respective wells.

190. A method according to claim 189 wherein in step (iii) the fluid is injected sequentially into the at least two of the respective wells.

191. A method according to any one of claims 186 to 190 wherein in step (iii) an injection time that the fluid is injected is recorded and in step (iv) a recovery time that the tracer material is recovered is recorded.

192. A method according to claim 191 wherein a residence time between the injection and recovery times is determined.

193. A method according to claim 192 wherein the residence time is input as a parameter, optionally a calibration parameter, into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.
194. A method according to any one of claims 186 to 193 wherein in step (iii) an injection time period during which the fluid is injected is recorded and in step (iv) a recovery time period during which the tracer material is recovered is recorded.
195. A method according to claim 194 wherein a time period relationship between the injection time period and the recovery time period is determined.
196. A method according to claim 195 wherein a variation of the time period relationship with time is determined.
197. A method according to claim 195 or claim 196 wherein at least one of the time period relationship or the variation of the time period relationship with time is input as a parameter, optionally a calibration parameter, into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.
198. A method according to any one of claims 186 to 197 wherein in step (iii) in a first injection operation a first tracer material is injected and subsequently in a second injection operation a second tracer material is injected, the first and second tracer materials having different identifiable DNA.
199. A method according to any one of claims 186 to 198 wherein in step (iii) the injected fluid comprises a known initial concentration of the tracer material and in step (iv) a final concentration of the recovered tracer material is recorded.
200. A method according to claim 199 wherein in step (iii) the known initial concentration of the tracer material varies with time and in step (iv) a final concentration, varying with time, of the recovered tracer material is recorded.
201. A method according to claim 199 or claim 200 wherein a concentration relationship between the initial and final concentrations is determined.
202. A method according to claim 201 wherein a variation of the concentration relationship with time is determined.

203. A method according to claim 201 or claim 202 wherein at least one of the concentration relationship or the variation of the concentration relationship with time is input as a parameter, optionally a calibration parameter, into a computer model of a production system including one or more oil or gas reservoirs or wells or any combination thereof.
204. A method according to any one of claims 186 to 203 wherein in step (iii) the fluid comprises a detectable indicator in addition to the tracer material.
205. A method according to claim 204 wherein the detectable indicator comprises at least one dye.
206. A method according to any one of claims 186 to 205 wherein the tracer material is encapsulated within a coating layer of the tracer particle and during the hydraulic fracturing operation the coating layer is degraded within the well to release the tracer material into the well.
207. A method according to claim 206 wherein the tracer material is encapsulated as a plurality of nanoparticles within the coating layer and during the hydraulic fracturing operation the coating layer is degraded within the well to release the nanoparticles into the well.
208. A method according to any one of claims 186 to 207 wherein in step (iii) the fluid is injected into an oil or gas well in an enhanced oil recovery (EOR) operation.
209. A method according to claim 208 wherein a plurality of the oil or gas wells is provided defining a central area therebetween, and in step (iii) a respective sample of the fluid is injected into a respective well of at least two of the respective wells, each sample having a respective tracer material therein.
210. A method according to any one of claims 153 to 209 wherein in the tracer particle the identifiable DNA is complexed with a complexing agent.
211. A method according to claim 210 wherein the complexing agent is a complexing polymer.
212. A method according to any one of claims 153 to 211 wherein the identifiable DNA is at least partly encapsulated by an encapsulating polymer in a nanoparticle.
213. A method according to claim 212 wherein the encapsulating polymer comprises at least one acrylate-, methacrylate- or styrene-based polymer.

214. A method according to claim 213 wherein the encapsulating polymer is a cross-linked polymer including a cross-linker.
215. A method according to claim 214 wherein the cross-linker is adapted to be chemically reduced by a reducing agent thereby to degrade the encapsulating polymer to release the DNA for analysis, optionally a disulfide cross-linker.

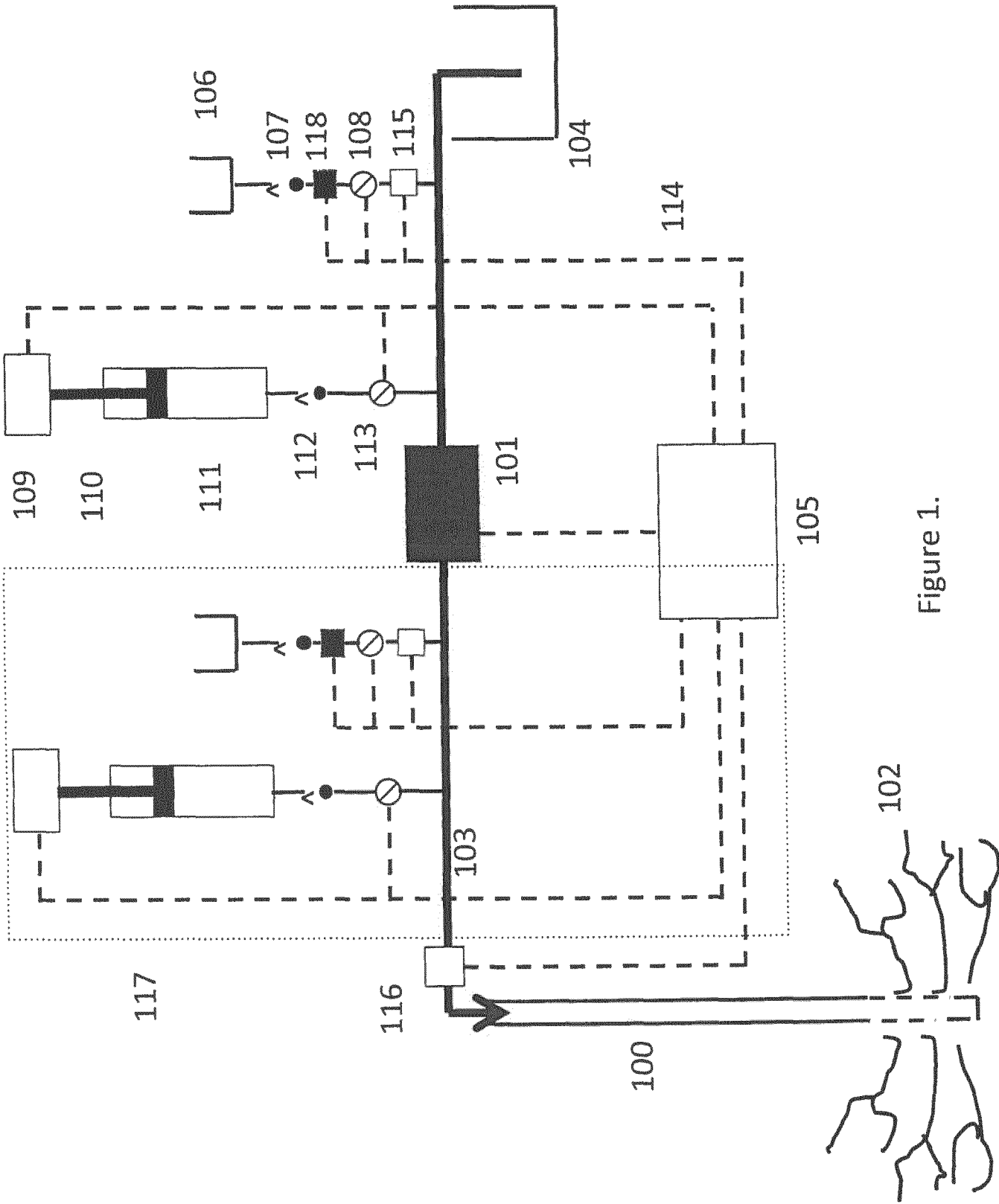


Figure 1.

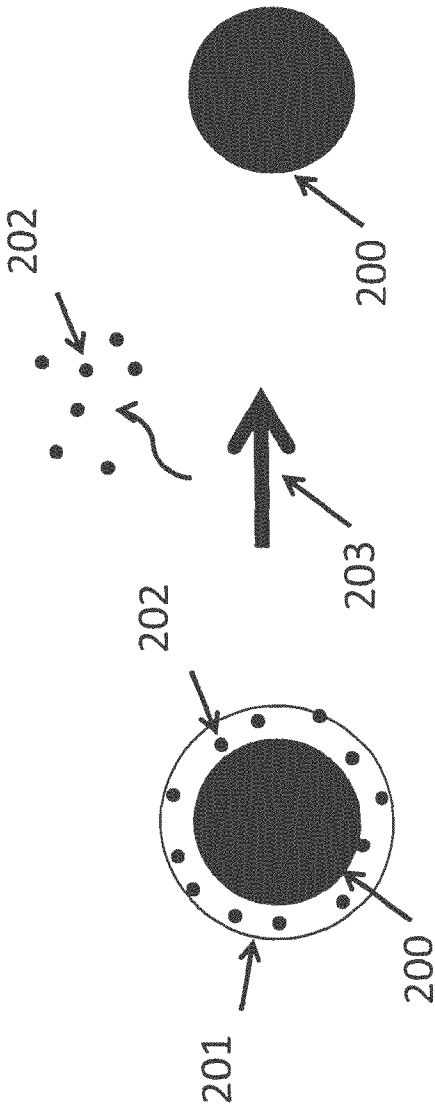


Figure 2a

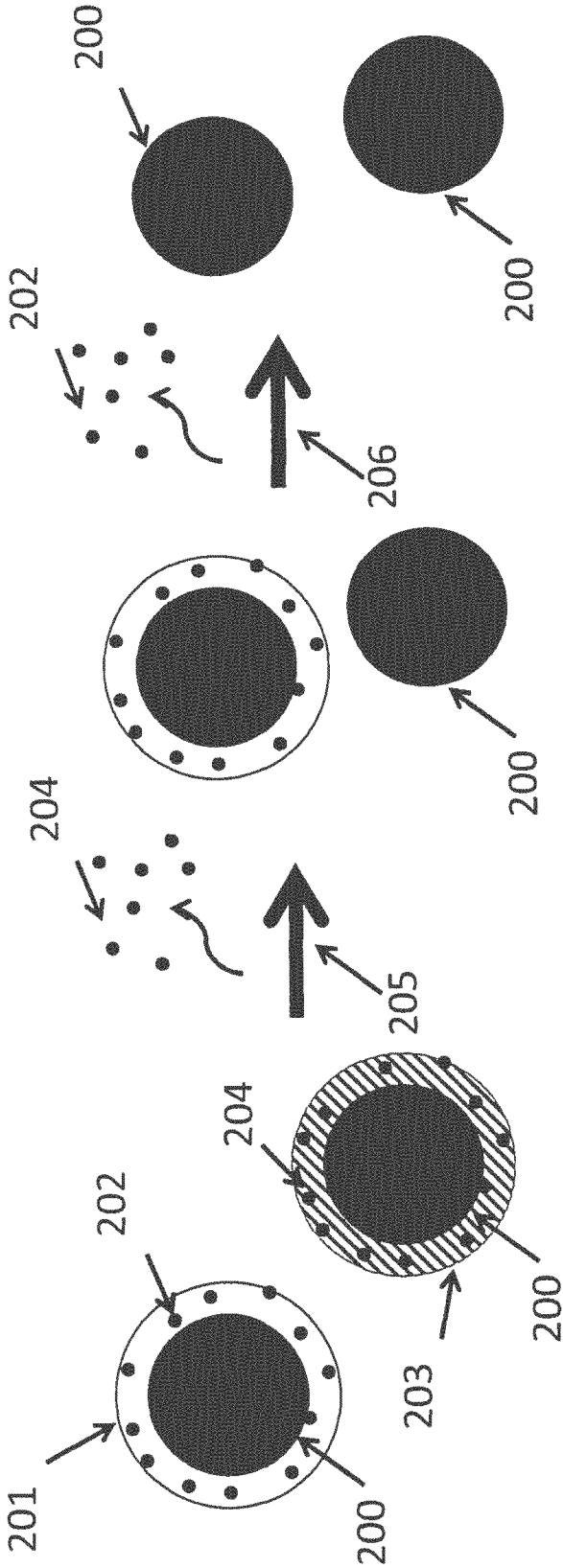


Figure 2b

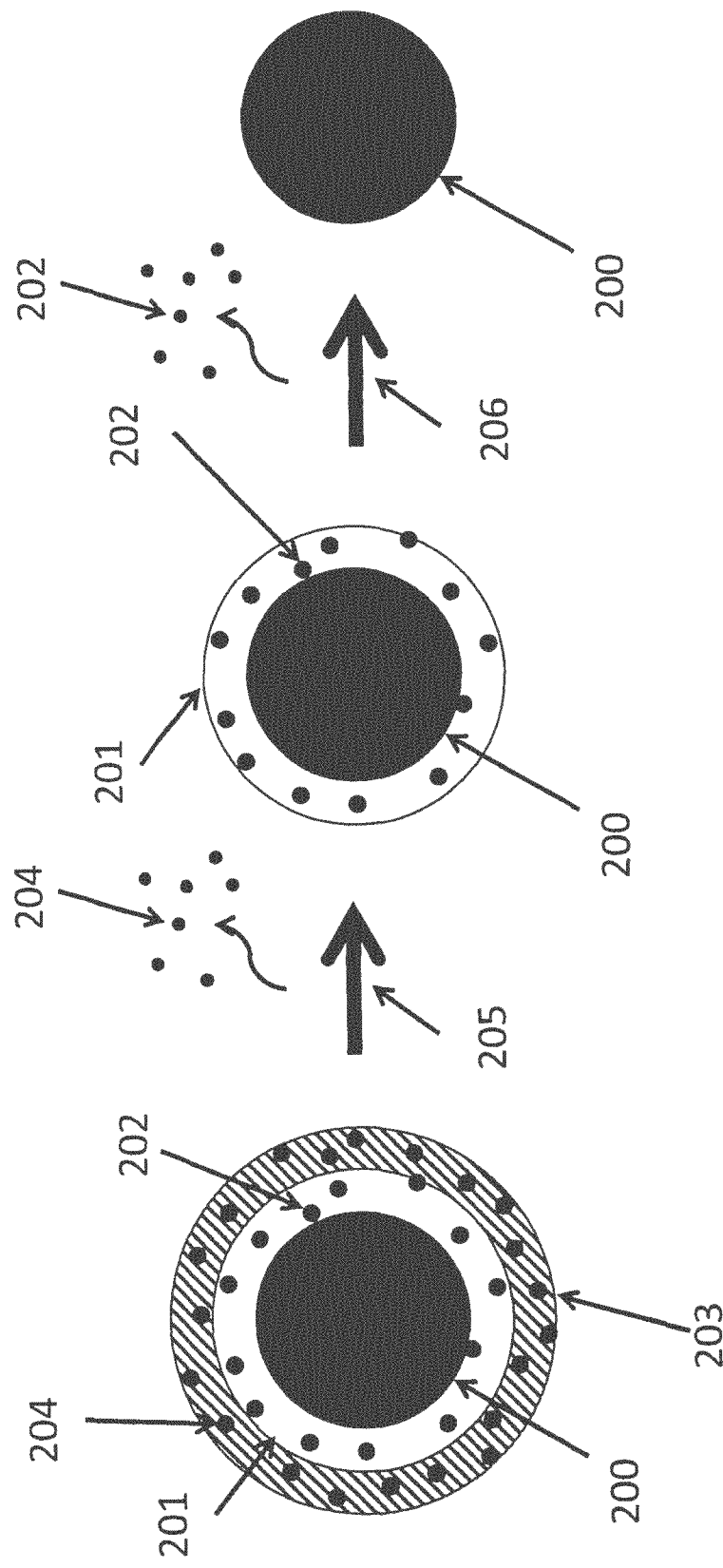


Figure 2c

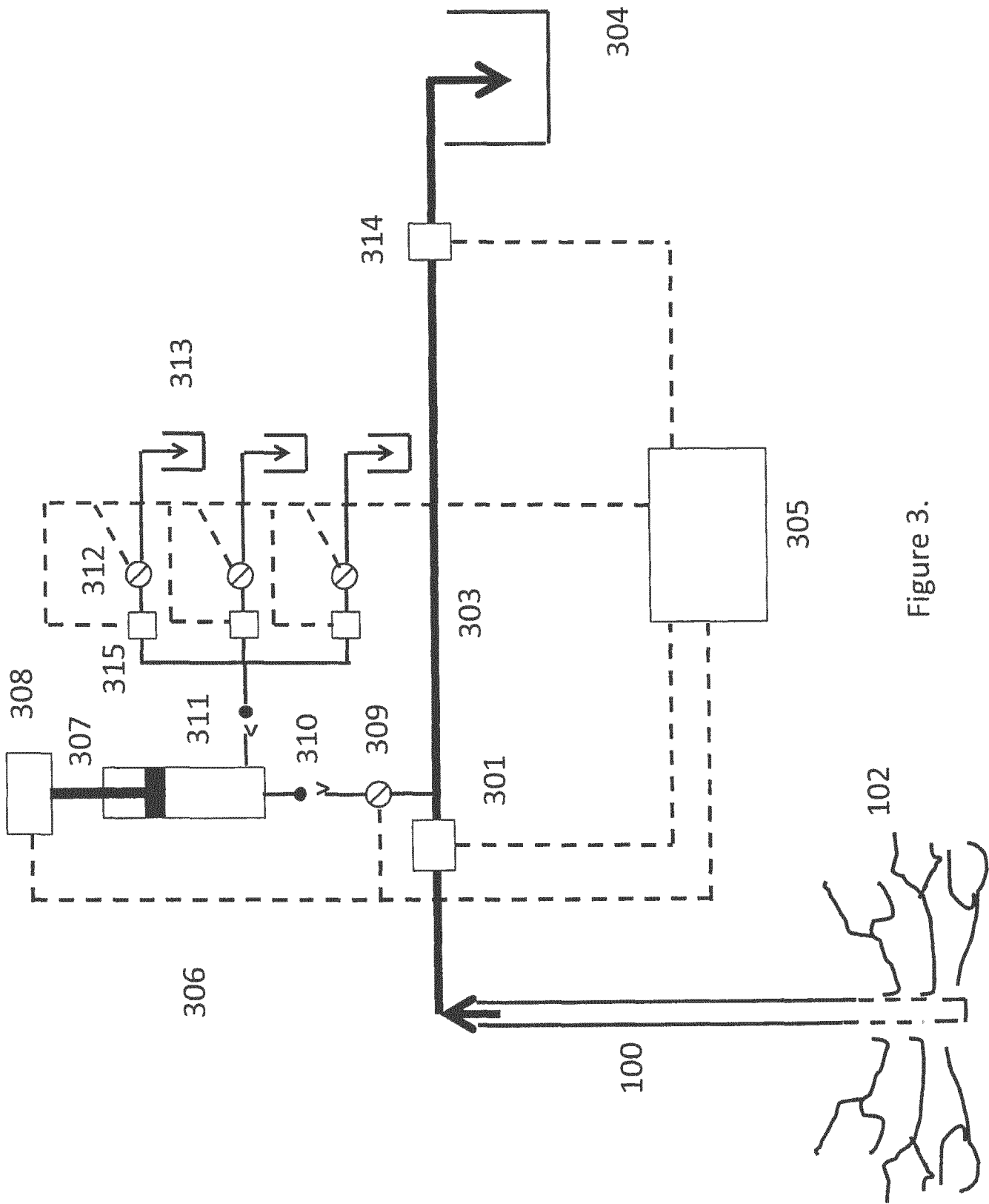


Figure 3.

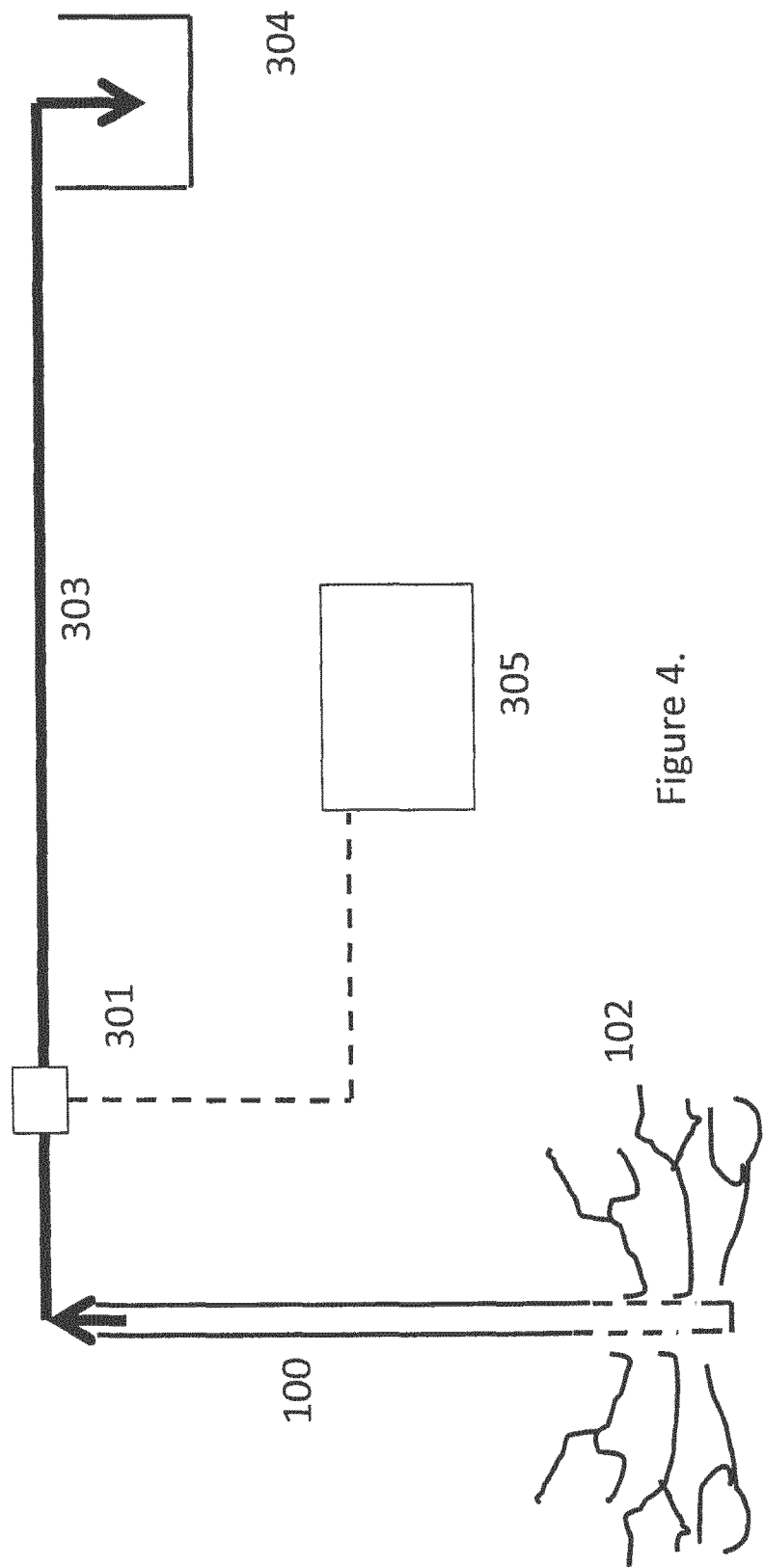


Figure 4.

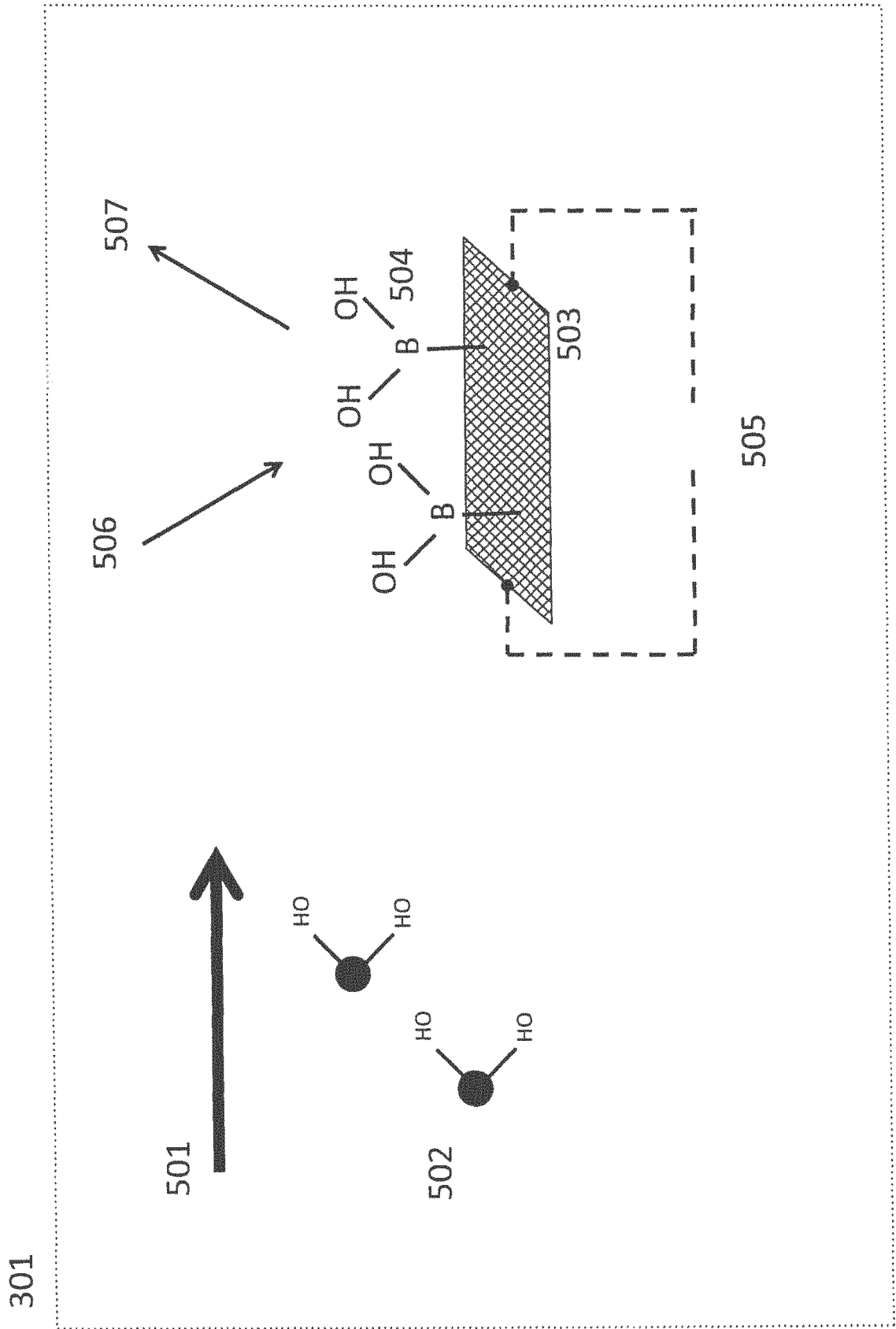


Figure 5.

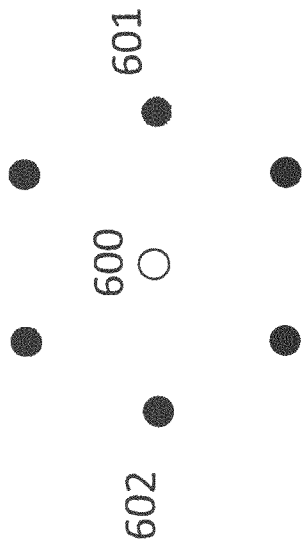


Figure 6a.

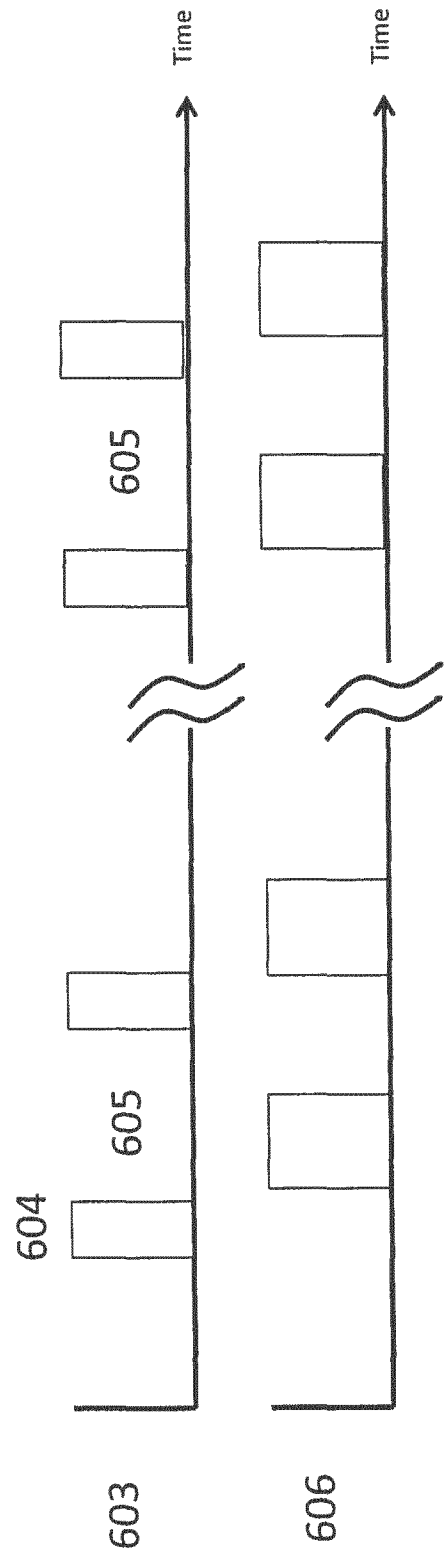


Figure 6b.

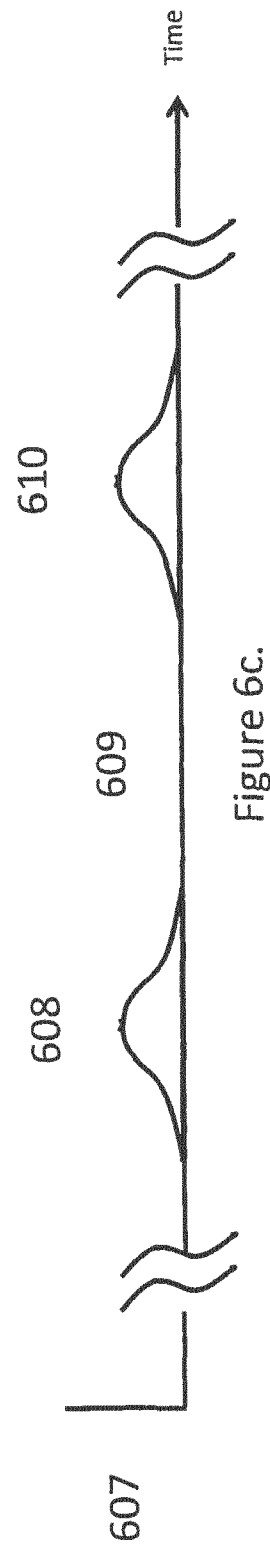


Figure 6c.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2015/067432

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K8/80 C12Q1/68 E21B47/10 C09K8/03
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K C12Q E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2014/144464 A2 (CARBO CERAMICS INC [US]) 18 September 2014 (2014-09-18) claims 1, 8-10, 31-37 -----	1,2, 10-17
X	GB 2 489 714 A (TRACESA LTD [GB]) 10 October 2012 (2012-10-10) cited in the application claims page 1 - page 6 page 11 - page 12 -----	1-24, 39-108, 186-215
X	WO 2012/136734 A1 (TRACESA LTD [GB]; MCCANN DOMINIC PATRICK JOSEPH [GB]; FORBES KEVIN JOH) 11 October 2012 (2012-10-11) cited in the application claims ----- -/-	1-24, 39-108, 186-215



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

21 December 2015

Date of mailing of the international search report

13/01/2016

Name and mailing address of the ISA/

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Authorized officer

Zimpfer, Emmanuel

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2015/067432

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/258743 A1 (BORTOLIN LAURA [US]) 14 October 2010 (2010-10-14) claims -----	1,10,39, 186
A	US 5 665 538 A (SLATER JAMES HOWARD [GB] ET AL) 9 September 1997 (1997-09-09) claims -----	1-24, 39-108, 186-215
A	WO 2007/132137 A1 (SCHLUMBERGER TECHNOLOGY BV [NL]; SCHLUMBERGER HOLDINGS; SCHLUMBERGER C) 22 November 2007 (2007-11-22) claims -----	1-24, 39-108, 186-215

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2015/067432

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of Item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-24, 186-215(completely); 39-108(partially)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-24, 186-215(completely); 39-108(partially)

claim 1 relates to a tracer particle for use in the exploration, production, transportation and/or storage of oil and/or gas, the tracer particle comprising a proppant material, a coating layer at least partially surrounding the proppant material and a tracer material within the coating layer, the tracer material having an identifiable DNA.

2. claims: 25-38, 186-215(completely); 39-108(partially)

claim 25 relates to a tracer particle in the form of a capsule comprising an outer shell encapsulating tracer material which comprises a plurality of nanoparticles having identifiable DNA.

3. claims: 109-137

Claim 109 relates to an apparatus for tracing fluid during the exploration, production, transportation and/or storage of oil and/or gas, the apparatus comprising an injector unit for injecting a pulse of fluid, containing at least one tracer particle, including tracer material having identifiable DNA, therein, into a supply of oil or gas; a monitoring unit for monitoring the supply of oil or gas to detect the fluid or any tracer material therein; a recovery unit for subsequently recovering at least some of the tracer material which was in the injected fluid, the recovery unit includes a recovery element having a surface adapted to bind chemically or physically to a surface of the tracer material to capture the tracer material on the recovery element; an analysis unit for analyzing any identifiable DNA in the tracer material, and a controller for controlling the operation of at least one of the injector unit, the monitoring unit, the recovery unit and the analysis unit or any combination thereof.

4. claims: 138-166

Claim 138 relates to a tracer nanoparticle for use in the exploration, production, transportation and/or storage of oil and/or gas, the tracer nanoparticle comprising a tracer material having an identifiable DNA, and at least one chemical moiety located in at least an outer surface of the tracer nanoparticle, the at least one chemical moiety comprising at least one protein, at least one antibody, and/or at least one hydroxyl moiety.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

5. claims: 167-185

Claim 167 relates to a method of tracing fluid during the exploration or production of oil and/or gas, the method comprising the steps of: (i) providing a tracer particle comprising a tracer material, the tracer material having an identifiable DNA; (ii) introducing the tracer particle into a fluid; (iii) injecting the fluid, containing the tracer particle therein, into a supply of oil or gas, and recording an injection parameter; (iv) subsequently recovering at least some of the tracer material which was in the injected fluid, and recording a recovery parameter; (v) analyzing any identifiable DNA in the tracer material; and (vi) before, simultaneously with, or after step (v), comparing the injection and recovery parameters to determine a property of the oil or gas reservoir and/or well and/or a property of the behaviour of the tracer particle or tracer material within the oil or gas reservoir and/or well.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/067432

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014144464	A2	18-09-2014	AU 2014229028 A1 17-09-2015
		CA 2904153 A1 18-09-2014	
		CN 105189921 A 23-12-2015	
		EP 2971497 A2 20-01-2016	
		US 2014262247 A1 18-09-2014	
		WO 2014144464 A2 18-09-2014	
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		CA 2832283 A1 11-10-2012	
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