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### (54) TRACER METHOD AND APPARATUS

VERFOLGUNGSVERFAHREN UND -VORRICHTUNG

PROCÉDÉ ET APPAREIL DE TRAÇAGE

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**Description**

**[0001]** The present invention relates to a method for tracing fluids, particularly fluids flowing within a well such as from an oil or gas reservoir, and to a perforation tool suitable for introducing a tracer into such a reservoir.

5 **[0002]** It is common in the oil exploration and recovery industry to place tracers within a well in order to determine the flow of fluid from the well or from a particular section of it. When the tracer is incorporated in the fluid flowing from the well, it may be detected in the fluid by analysis of the fluid arriving at the well-head. For example, US 3,623842 describes a method of determining fluid saturations in reservoirs by injecting at least two tracers having different partition coefficients between fluid phases (e.g. oil and water) into the formation and monitoring the appearance of the two tracers in the 10 produced fluids. This example uses ethyl acetate as a tracer chemical. Radioactive tracers have been widely used for many years in well-monitoring applications. As an example, see US 5,077,471, in which radioactive tracers are injected into a perforated well-bore, sealed and then monitored for decay to indicate the fluid flow from the formation. EP 0816631-A describes a procedure to determine the inflow of oil and/or gas from a subterranean oil and/or gas reservoir by placing 15 traceable material, preferably different radioactive isotopes, into different zones of the reservoir. An example is provided of shooting radioactive isotopes into a reservoir using a perforator gun.

20 **[0003]** One problem encountered with the use of radioactive tracers is that their transport and use is highly regulated, leading to greater expense and difficulty with their use. In addition, it has become quite common to use tracers associated with a perforation tool, in which the tracer is fired by explosive devices located around the tool into the formation to 25 perforate the formation and thereby to embed the tracer in the formation. Since explosive devices are also highly controlled, it has become very difficult to arrange the transport of devices incorporating both radioactive sources and explosives. Although non-radioactive tracers, i.e. chemical tracers, may be used, these require careful selection to ensure that they are sufficiently soluble in the phase to be monitored and that they are readily detectable at low concentrations. The high limit of detection of many chemicals makes them unsuitable for use as tracers. US 4,755,469 describes the 30 use of rare metal tracers for tracing oil and associated reservoir fluids by mixing an oil-dispersible rare metal salt with oil or an oil-like composition, injecting the dissolved tracer composition it into a subterranean reservoir and analysing oil fluids produced from a different part of the reservoir for the presence of the rare metal to determine whether the oil mixed with the tracer has been produced from the reservoir.

**[0004]** It is an object of the present invention to provide a tracer and a method of monitoring fluids flowing from a reservoir using the tracer which overcomes some of the problems with the existing tracers and methods.

35 **[0005]** According to the invention, we provide a method of monitoring the flow of fluid within or from a reservoir comprising the steps of inserting in said reservoir a solid non-radioactive tracer comprising at least one metal selected from caesium, niobium, tantalum, tellurium, terbium, lanthanum, gold, iridium, osmium, silver, platinum, palladium, rhenium, ruthenium, rhodium, hafnium, indium a metal of the Lanthanide series of the periodic table, or a salt thereof, thereafter collecting a sample of fluid within or flowing from the reservoir and analysing said sample to determine the amount of said tracer contained in the sample. From the presence or absence of tracer in the sample, its amount and other parameters such as sample size, timing of the sample collection etc, information about the fluid flow within the reservoir may be gathered. The reservoir is normally a subterranean oil and/or natural gas reservoir. The fluid flowing within the reservoir normally contains oil, natural gas, water and solids such as sand or other particles.

40 **[0006]** According to a second aspect of the invention we provide a perforation tool comprising an elongate body having a central longitudinal axis, a control means, deployment means and at least one explosive charge mounted on or within said body and associated with detonation means, said charge being arranged to direct energy explosively, outwardly, and, preferably transversely, along a path with respect to the elongate body upon detonation, and at least one tracer material mounted on or within said body within the path of said explosive energy, **characterised in that** the tracer material comprises at least one non-radioactive metal selected from caesium, niobium, tantalum, tellurium, terbium, lanthanum, gold, iridium, osmium, silver, platinum, palladium, rhenium, ruthenium, rhodium, hafnium, indium a metal of the Lanthanide series of the periodic table, or a salt thereof..

45 **[0007]** The tracer comprises at least one non-radioactive metal selected from caesium, niobium, tantalum, tellurium, terbium, lanthanum, gold, iridium, osmium, silver, platinum, palladium, rhenium, ruthenium, rhodium, hafnium, indium a metal of the Lanthanide series of the periodic table, or a salt thereof. The metals of the Lanthanide series comprise the 50 elements of atomic numbers from 57 to 71. Preferred metals include niobium, tantalum, tellurium, terbium, europium, platinum and rhodium, and especially preferred are niobium, tantalum, tellurium, terbium and europium. These metals are not naturally abundant and have a low detection limit using standard elemental analysis methods such as inductively-coupled plasma-mass spectroscopy (ICP-MS).

55 **[0008]** Many of the metals naturally contain more than one isotope. By non-radioactive, we mean that the metals used in the tracer do not contain a greater proportion of radioactive isotopes than found in the naturally occurring metal, i.e. they have not been enriched with radioactive isotopes. Some of the metals may contain unstable radioactive isotopes in their natural state but the emission of radioactivity is very low, and they are unsuitable for use as radioactive tracers at the dilutions typically used without enrichment with one or more radioactive isotopes. Normally for use as a radioactive

tracer a metal is treated, e.g. by bombardment with neutrons in a nuclear reactor, to enrich the composition of isotopes with unstable, radioactive isotopes which can emit detectable radiation. The metals used in the tracers of the present inventive method may have a composition of isotopes which is not naturally occurring, by enrichment with one or more stable non-radioactive isotopes to assist identification of the metal, particularly by mass-spectrometry.

5 [0009] In one preferred embodiment, the tracer or tracers may be formed of the selected metal or metals in elemental form. Alternatively the tracer may be supplied as salts of the metals. When used as salts, inorganic anions are preferred, particularly, a low-mass anion such as nitride or carbide in order to increase the amount of tracer metal in a given mass of tracer composition.

10 [0010] A tracer in elemental form may be conveniently supplied as a discrete tracer unit such as a disc, wire or rod or as a coating for placement in or attachment to a reservoir perforator gun (perforation tool). Alternatively the tracer metal may be moulded to fit around an explosive charge. The salts may be supplied as pressed discs or in another form. More than one metal may be used in a tracer. When more than one metal is used as a tracer they may be simply mixed or alloyed. Alternatively more than one discrete tracer unit, e.g. metallic disc, may be used in the same location or different tracers may be placed in different locations.

15 [0011] The tracer may take the physical form of a moulded metal shape such as a disc, wire or rod or may comprise finely divided particles of metal or as a salt of the metal. The particles may be formed into a shape, such as a tablet or disk, e.g. by pressing, extruding, granulating or other method, optionally using a binder. The tablet may further comprise other materials such as a diluent (i.e. a non-traceable material) to add mass, and/or a dispersant to aid dispersal and / or dissolution of the particles into the fluid to be traced. The tablet or other shape may be encased in a protective coating, preferably of a soluble or permeable material.

20 [0012] For insertion of a tracer by means of a perforator gun, it is preferred to form the tracer metal into a disc for placement into a perforation gun apparatus, either in an external scallop or in close proximity to the explosive charge. Typically a disc may contain from about 0.1 g - 20g especially 5 - 20 g of metal, preferably from about 8 to 12 g. The tracer may be associated with each explosive charge or only some of them. Preferably the amount of tracer used in a well section provides from about 20 to about 500 g (more preferably between about 50 and 200 g) of tracer metal.

25 [0013] The sample of fluid may be taken from the top of the well or may be withdrawn from within a well using a suitable well tool. The sample may be analysed by any suitable means to determine the amount of tracer present. There are many suitable methods for the detection and measurement of metals in a sample by elemental analysis. One suitable method is inductively coupled plasma mass spectrometry (ICP-MS) calibrated for the metal used in the tracer. The 30 collected fluid sample may be aspirated into the plasma, optionally after a treatment to separate the phases or to concentrate the sample. Alternatively, when the sample is a hydrocarbon such as crude oil, the sample may be ashed and then extracted into acid which may then be introduced into the plasma. Inductively-coupled plasma atomic emission spectrometry (ICP-AES) is also a suitable elemental analysis method to determine the metal tracer content of the sample. We have found that it is beneficial to dilute the sample in a suitable solvent, preferably with the addition of a complexing 35 agent. The complexing agent maintains the tracer metals in solution and avoids loss of tracer on surfaces within the analytical apparatus. When metal tracers stick to surfaces within the apparatus, they may be leached into successive samples passing through the apparatus and lead to inaccurate estimates of tracer within the sample. Any suitable complexing agent may be used, provided it does not interfere with the analysis of the tracers and forms a stable complex with the metal in the selected solvent. Suitable complexing agents include quaternary ammonium compounds. For the 40 analysis of tracers in organic solution we have found that quaternary ammonium compounds having long-chain or bulky alkyl groups are very suitable, for example methyltriocetylammonium chloride, sold commercially as ALIQUAT™ 336.

45 [0014] In a preferred method for analysing an oil sample for a tracer, an internal standard is added to the sample which is believed to contain the tracer and diluted with a solvent containing a complexing agent. The resulting solution is then analysed by ICP-MS configured for organics operation.

[0015] Alternatively, X-ray fluorescence spectroscopy may be used to determine the amount of fluorescence emitted by the sample at one or more characteristic frequencies when irradiated by X-rays. All of these methods are widely used in analysis and may be operated by the skilled person in a suitable manner. Alternative methods of elemental analysis may also be used, as would be known to the skilled analyst. Such methods may include chemical analysis, atomic absorption spectroscopy, the use of metal sensitive electrodes, voltammetry etc but these methods are likely to be less sensitive than the preferred instrumental analysis methods described above and so are less preferred.

50 [0016] It is preferred to analyse a blank sample from the well (i.e. a sample taken before tracer was inserted in the reservoir) in order to determine the amount of the selected tracer metal occurring naturally in the fluids. When the tracer is to be detected in a water-based fluid such as produced water, for example, then the sample preparation may differ from that used for an organic sample: e.g. by evaporating the sample rather than ashing.

55 [0017] The above-described methods are generally capable of quantitatively determining the amount of metal found in a sample, with suitable calibration. However, it should be recognised that the tracer technique itself may not be quantitative because, especially when the tracer is forced into the reservoir formation by a perforation gun, at least some of the metal may stick to the formation in an unpredictable manner. Therefore the method may be most useful for

determining the presence or absence of flow from a particular region of the reservoir.

[0018] The tracer method of the invention may be varied according to conventional methodologies used in the industry. Therefore, two or more tracers may be combined in a predetermined ratio in order to produce a unique tracer composition for marking a particular well or section of a well. It may be desired to determine the flow of tracer from a particular part of a well or reservoir. In this case a single reservoir may be marked by inserting different tracers or combinations of tracers in different locations in order to determine the part of the reservoir from which a particular sample has originated or flowed through.

[0019] The tracer may be inserted in the reservoir by one or more different methods. A preferred method comprises associating the tracer with a part of a perforation tool or perforation gun. The placement of tracers into the formation using a perforation tool (also known as a perforation gun) is already known. A perforation tool is used in the oil and gas drilling, exploration and recovery industry for perforating a well, i.e. for forming channels or perforations extending from a well-bore into the reservoir formation. Each channel or perforation is formed by detonating an explosive charge carried on a tool located in the well. The explosive energy is directed into the well casing (if the well has been cased) or the side of the well to penetrate the formation so that the well casing or well bore side is perforated allowing communication with the formation in the region of the tool. The perforations form channels through which reservoir fluids may flow out of the formation and into the well bore, thereby to flow to the surface of the well for recovery. Perforation tools vary in their size and design according to the result they are to achieve and any description herein of perforation tools is given as general background and not intended to limit the invention. Perforation tools are equipment already known and used in the oil exploration industry, and so a skilled designer of such tools is able to construct a tool suitable for use in the present invention. The tool is typically of generally cylindrical shape and has a length typically of between about 0.5 and about 10 metres. Typically the perforation tool carries more than one charge, usually arranged around the circumference of the tool or gun. The number of charges carried on a perforation tool varies but typically may be between about 2 and about 12 charges per foot (300 mm), normally arranged in a pattern, e.g. approximately helically, along the length of the tool. The explosive charge, detonation means, deployment means and control means comprise materials and apparatus which are known in the industry. For example, the charge is normally shaped to direct the explosive energy along the desired path relative to the body of the perforation tool. The detonator is usually an electrically operated detonator. Control means may comprise a microprocessor and associated control program mounted within the perforation tool or an associated tool or the tool may be controlled directly by means of signals carried to the tool from an operator, normally located at the head of the well. The signals may be carried along a cable connecting the tool and the well-head. The tool is normally deployed by lowering it down a well suspended on a wire or string before, during or after completion of a well.

[0020] The tool generally has an outer sleeve covering the explosive charges. When a perforation tool is used to insert tracer into a formation, the tracer may be placed into indentations or "scallops" formed in the outer sleeve, usually directly over one or more of the explosive charges carried by the tool. The tracer compounds may be held in place by an adhesive or a covering film, such as an epoxy resin covering. Alternatively the tracer compounds may be located within the outer sleeve or casing of the perforation tool, for example in contact with an inner sleeve within the gun. It is preferred that the tracer materials are not placed in contact with the explosive charges in order to avoid destabilising the charges by redirecting the angle of the blast. The tracer is therefore placed spaced away from the charge in the path of the blast so that at least some of the tracer material is carried into the reservoir formation with the explosive gases when the charge is detonated. It is likely that some of the tracer is vaporised in the explosion and then condenses within the formation. At least some of the tracer particles are then carried out of the formation with the flow of fluids released by the perforation of the formation by the explosive charge. The tracer or tracers may be placed in the gun or perforation tool in the form of shaped units as described hereinbefore or coated onto a part of a perforator gun. Alternatively the tracer metal may be moulded to fit around an explosive charge.

[0021] It is not necessary to dissolve the tracer in the fluid to be traced; it is sufficient in many circumstances to disperse particles of the metal or salt in the fluid so that the finely divided metal particles flow with the fluid. A metal salt tracer may be selected to be soluble in the fluid which is to be traced. For example when the tracer is for use in monitoring flows of oil in an oil well, then an oil-soluble metal salt may be selected, e.g. a salt of an organic acid, particularly a long-chain fatty acid. When the tracer is for use in a water-based system, e.g. for tracing water pumped into a well, then it is preferred to use a water-soluble salt of the tracer metal(s) such as a sulphate, nitrate or halide. Alternatively a solid tracer comprising a soluble salt of the metal is placed in the well and is then dissolved in the water flowing within the well. The method of the invention is for the placement of solid tracers comprising non-radioactive metals in a reservoir for tracing the flow of fluids in and from a well bored into the reservoir. It is known from US 5,711,900 and US 6,001,280 to use as a tracer a solution of a gadolinium salt of a carboxylic acid. The deployment of tracer solutions as disclosed in those references is not within the scope of the present invention.

[0022] The invention will be further described in the following examples with reference to the drawing which is:

Figure 1 a graph showing the concentration of Nb and Ta found in a sample of reservoir fluids against time when

the sample was taken.

#### Preparation of reagents

5 [0023] The following reagents were used:

ICP standard solutions of 1000 mg/ml Nb, Ta, Y, Ti, La, (supplied by Inorganic ventures, Aldrich and VWR)  
 Multi element precious metals standard containing 100 mg/ml Au, Ir, Os, Pt, Pd, Pt, Re, Rh and Ru (supplied by Alfa-Aesar).  
 10 Dilution solution for stock standards, 10% w/v Aliquat™ 336, 10% v/v ethyl hexanol in MIBK  
 Dilution solution for samples, 1% w/v Aliquat 336, 5% v/v ethyl hexanol in Lotoxane™ solvent.

[0024] 1 µg/ml stock standards were prepared by diluting 50 µl aliquots of the 1000 µg/ml and 500 µl of the 100 µg/ml ICP standards to 50 ml with stock standard dilution solution.

15 [0025] The following 1 mg/ml combined stock solutions were prepared:

- 1) Nb,+Ta
- 2) La + In
- 3) Au, Ir, Os, Pt, Pd, Pt, Re, Rh + Ru
- 4) Y + Ti internal standard

[0026] A 0.1 mg/ml combined standard was the prepared by combining 1 ml aliquots of stock solutions 1, 2 and 3 and diluting to 10 ml with stock standard dilution solution.

[0027] Instrumentation: ICP-MS, Thermo X Series II fitted with organics kit, peltier cooled spray chamber, micromist low flow nebuliser (Glass Expansion), extra mass flow controller for addition of oxygen into the plasma and platinum cones. The instrument was initially set up with a standard aqueous introduction system and a detector cross-calibration and full system tune were preformed. An instrument performance check was then performed to confirm that the instrument was performing within the manufacturers acceptance limits. The organics kit was then fitted and the instrument stabilised on isopropanol. A blank solution containing internal standard was aspirated. The oxygen flow was adjusted until the green carbon emission was removed and the ICP-MS optics were then optimised on the low and high mass internal standards.

#### Calibration

35 [0028] High level calibration standards were prepared by combining aliquots of stock solutions 1, 2 and 3, plus 500 µl of internal std solution and 1 g of base oil and diluting to 10 g with sample dilution solution. Low level calibration standards were prepared by adding aliquots of the 0.1 µg/ml combined standard, 1 g of base oil and 500 µl of internal std solution and diluting to 10 g with sample dilution solution. The instrument was calibrated using the prepared high-level and low-level calibration standards. Instrument response was linear over the calibration range 0 - 20 ng/g with a relative standard deviation of less than 2%.

#### Detection limits

40 [0029] The detection limits for the metals was determined as 3x standard deviation (limit of detection, LOD) and 10x standard deviation (limit of quantification, LOQ) of the results of ten repeated determinations of a measuring a 100 pg/g standard solution. The highest LOD and LOQ was found for La at 35 pg/g and 117 pg/g respectively.

#### Example 1

50 [0030] A 1g sample of crude oil was spiked with 50µl of 0.1 µg/ml combined standard. 500 µl of internal standard solution was added and diluted to 10 g with sample dilution solution. This gives a spike of 0.5 ng / g in the final solution (equivalent to 5 ng / g in the 1g sample). To establish a base level an un-spiked sample was prepared in the same way. The samples were analysed using the calibrated ICP-MS instrument and the results are shown in Table 1.

55 [0031] The concentration of each of the metals found in the background (i.e. the un-spiked sample) is shown together with the percentage of added metal tracer found in the spiked sample after subtraction of the background level. The results show that recovery of the metal tracer elements was between 80 and 110 %. Values greater than 100% are believed to be caused by the spiked sample responding better in the plasma than the calibration samples, an effect which may be due to the different viscosity of the sample and calibration solutions.

Table 1

Element	Background (pg/g)	Spike Recovery (%)
Nb	718	82
Ru	41	103
Rh	67	105
Pd	521	105
In	78	105
La	8763	104
Ta	44	95
Re	38	107
Os	26	108
Ir	104	84
Pt	23	110
Au	121	112

Example 2

**[0032]** 12g of niobium carbide powder was mixed with a microcrystalline wax binder and formed into 40 disk-shaped tablets, each approximately 10mm diameter and 2mm thick by pressing. The tablets were placed into indentations, known as scallops, in the outer surface of the casing of a perforation tool and covered in an epoxy material. A second batch of 40 tablets containing a total of 12g of tantalum carbide mixed with the wax binder was prepared in the same way and the tablets were placed into the scallops of a second perforation tool. The perforation tools were of a standard type, each being provided with a plurality of explosive charges arranged to fire outwardly from the perforation tool in a predetermined direction upon operation of the tool. The perforation tools were placed down a well into different locations in the formation of an oil reservoir and fired to perforate the formation. When the reservoir fluids had reached the surface, samples of the reservoir fluid were collected every 30 minutes. The samples were later analysed using the ICP-MS method described above. The results are plotted in Figure 1 as the concentration of Nb and Ta found in a sample against time when the sample was taken. The plot shows that both Nb and Ta have been detected confirming that both perforation tools fired and that fluid is flowing up the well from the locations of each of the perforation tools. This confirms that the perforation tool successfully perforated the formation and that fluid flowed from fissures in the formation opened by the operation of the tool. The Ta peak appears to lag behind the Nb peak by a short time and this is believed to confirm that the tool containing the Ta tracer was placed further from the well-head than the tool containing the Nb tracer.

**Claims**

1. A method of monitoring the flow of fluid within or from a reservoir comprising the steps of:
  - inserting in said reservoir a solid tracer by means of a perforation tool;
  - thereafter collecting a sample of fluid within or flowing from the reservoir and analysing said sample to determine the amount of said tracer contained in the sample, **characterised in that** the solid tracer comprises at least one non-radioactive metal selected from caesium, niobium, tantalum, tellurium, terbium, lanthanum, gold, iridium, osmium, silver, platinum, palladium, rhenium, ruthenium, rhodium, hafnium, indium, a metal of the Lanthanide series of the periodic table, or a salt of said at least one non-radioactive metal.
2. A method as claimed in claim 1, wherein the tracer comprises caesium, niobium, tantalum, tellurium, terbium, europium, platinum or rhodium or a salt thereof.
3. A method as claimed in claim 1 or claim 2, wherein the tracer comprises a water soluble salt of at least one of said

metals.

4. A method as claimed in claim 1 or claim 2, wherein the tracer comprises a hydrocarbon-soluble salt of at least one of said metals.

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5. A method as claimed in claim 1 or claim 2, wherein the tracer comprises at least one of said metals in elemental form.

6. A method as claimed in any one of the preceding claims, wherein the tracer is in the form of finely divided particles of metal or of a salt of the metal.

10

7. A method as claimed in claim 6, wherein the particles are formed into a shaped unit.

8. A method as claimed in any one of the preceding claims, wherein the reservoir is a subterranean oil and/or natural gas reservoir.

15

9. A perforation tool comprising:

- an elongate body having a central longitudinal axis;

- a control means;

- deployment means; and

- at least one explosive charge mounted on or within said body and associated with detonation means, said charge being arranged to direct energy explosively and outwardly from the elongate body upon detonation, and at least one solid tracer material mounted on or within said body within the path of said explosive energy, **characterised in that** the solid tracer material comprises at least one non-radioactive metal selected from caesium, niobium, tantalum, tellurium, terbium, lanthanum, gold, iridium, osmium, silver, platinum, palladium, rhenium, ruthenium, rhodium, hafnium, indium, a metal of the Lanthanide series of the periodic table, or a salt of said at least one non-radioactive metal.

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10. A perforation tool as claimed in claim 9, wherein the tracer comprises caesium, niobium, tantalum, tellurium, terbium, europium, platinum and rhodium or a salt thereof.

30

11. A perforation tool as claimed in claim 9 or claim 10, wherein the tracer comprises a water-soluble salt of at least one of said metals.

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12. A perforation tool as claimed in claim 9 or claim 10, wherein the tracer comprises a hydrocarbon-soluble salt of at least one of said metals.

13. A perforation tool as claimed in claim 9 or claim 10, wherein the tracer comprises at least one of said metals in elemental form.

40

14. A perforation tool as claimed in any of claims 9 - 13, wherein the tool comprises an outer sleeve covering the explosive charges and wherein the tracer is located in one or more indentations formed in the outer sleeve aligned with one or more of the explosive charges.

45

15. A perforation tool as claimed in any of claims 9 - 13, wherein the tracer is located spaced away from a charge between said charge and an outer sleeve of said tool in the intended path of the explosive blast so that at least some of the tracer material is carried into the reservoir formation with the explosive gases when the charge is detonated.

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## Patentansprüche

1. Verfahren zur Überwachung des Fluidstroms innerhalb einer Lagerstätte oder aus einer Lagerstätte, das die Stufen umfasst:

55

- Einführen eines festen Tracers mit Hilfe eines Perforationswerkzeugs in die Lagerstätte,
- anschließendes Sammeln einer Probe eines Fluids in der Lagerstätte oder eines aus der Lagerstätte ausströmenden Fluids und Analysieren der Probe, um die Menge des genannten Tracers, die in der Probe vorhanden

ist, zu bestimmen,

**dadurch gekennzeichnet, dass** der feste Tracer wenigstens ein nicht-radioaktives Metall umfasst, das ausgewählt ist aus Cäsium, Niob, Tantal, Tellur, Terbium, Lanthan, Gold, Iridium, Osmium, Silber, Platin, Palladium, Rhenium, Ruthenium, Rhodium, Hafnium, Indium, einem Metall der Lanthanidenreihe des Periodensystems, oder ein Salz des genannten wenigstens einen nicht-radioaktiven Metalls.

5        2. Verfahren nach Anspruch 1, wobei der Tracer Cäsium, Niob, Tantal, Tellur, Terbium, Europium, Platin oder Rhodium oder ein Salz davon umfasst.

10      3. Verfahren nach Anspruch 1 oder Anspruch 2, wobei der Tracer ein wasserlösliches Salz von wenigstens einem der genannten Metalle umfasst.

15      4. Verfahren nach Anspruch 1 oder Anspruch 2, wobei der Tracer ein kohlenwasserstofflösliches Salz von wenigstens einem der genannten Metalle umfasst.

20      5. Verfahren nach Anspruch 1 oder Anspruch 2, wobei der Tracer wenigstens eines der Metalle in elementarer Form umfasst.

25      6. Verfahren nach irgendeinem der vorausgehenden Ansprüche, wobei der Tracer in Form fein verteilter Teilchen des Metalls oder eines Salzes des Metalls vorliegt.

30      7. Verfahren nach Anspruch 6, wobei die Teilchen zu geformten Einheiten geformt sind.

25      8. Verfahren nach irgendeinem der vorausgehenden Ansprüche, wobei die Lagerstätte eine unterirdische Öl- und/oder Erdgas-Lagerstätte ist.

35      9. Perforationswerkzeug, das umfasst:

- einen langgestreckten Körper mit einer zentralen Längsachse;

- eine Steuereinrichtung;

- Einsatzmittel; und

- wenigstens eine Explosivladung, die auf dem oder innerhalb des genannten Körpers montiert ist und mit Zündmitteln assoziiert ist, wobei die genannte Ladung so angeordnet ist, dass bei der Zündung Energie explosionsartig und von dem langgestreckten Körper nach außen gerichtet wird, sowie wenigstens ein festes Tracermaterial, das im Weg der genannten Explosionsenergie auf dem oder innerhalb des genannten Körpers montiert ist,

**dadurch gekennzeichnet, dass** das feste Tracermaterial wenigstens ein nicht-radioaktives Metall umfasst, das ausgewählt ist aus Cäsium, Niob, Tantal, Tellur, Terbium, Lanthan, Gold, Iridium, Osmium, Silber, Platin, Palladium, Rhenium, Ruthenium, Rhodium, Hafnium, Indium, einem Metall der Lanthanidenreihe des Periodensystems, oder ein Salz des genannten wenigstens einen nicht-radioaktiven Metalls.

40      10. Perforationswerkzeug nach Anspruch 9, wobei der Tracer Cäsium, Niob, Tantal, Tellur, Terbium, Europium, Platin und Rhodium oder ein Salz davon umfasst.

45      11. Perforationswerkzeug nach Anspruch 9 oder Anspruch 10, wobei der Tracer ein wasserlösliches Salz von wenigstens einem der Metalle umfasst.

50      12. Perforationswerkzeug nach Anspruch 9 oder Anspruch 10, wobei der Tracer ein kohlenwasserstofflösliches Salz von wenigstens einem der genannten Metalle umfasst.

55      13. Perforationswerkzeug nach Anspruch 9 oder Anspruch 10, wobei der Tracer wenigstens eines der genannten Metalle in elementarer Form umfasst.

14. Perforationswerkzeug, wie es in irgendeinem der Ansprüche 9 bis 13 beansprucht wird, wobei das Werkzeug eine äußere Hülse umfasst, die die Explosivladungen überdeckt, und wobei der Tracer in einer oder mehreren Vertiefungen angeordnet ist, die in der äußeren Hülle ausgebildet sind und mit einer oder mehreren der Explosivladungen fluchten.

15. Perforationswerkzeug nach irgendeinem der Ansprüche 9 bis 13, wobei der Tracer in einem Abstand entfernt von einer Ladung zwischen der Ladung und einer äußeren Hülse des genannten Werkzeugs im geplanten Weg Explosionsdruckwelle angeordnet ist, so dass wenigstens etwas von dem Tracermaterial mit den Explosionsgasen in die Lagerstättenformation mitgerissen wird, wenn die Ladung gezündet wird.

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## Revendications

1. Procédé pour surveiller l'écoulement de fluide au sein, ou à partir, d'un réservoir comprenant les étapes consistant à :
  - insérer dans ledit réservoir un traceur solide au moyen d'un outil de perforation ;
  - recueillir ensuite un échantillon de fluide à l'intérieur, ou s'écoulant, du réservoir et analyser ledit échantillon pour déterminer la quantité dudit traceur contenue dans l'échantillon,

15      **caractérisé en ce que** le traceur solide comprend au moins un métal non radioactif sélectionné dans le groupe consistant en césium, niobium, tantale, tellure, terbium, lanthane, or, iridium, osmium, argent, platine, palladium, rhénium, ruthénium, rhodium, hafnium, indium, un métal des lanthanides du tableau périodique, ou un sel dudit au moins un métal non radioactif.
2. Procédé selon la revendication 1, dans lequel le traceur comprend du césium, niobium, tantale, tellure, terbium, europium, platine ou rhodium ou un sel de ceux-ci.
3. Procédé selon la revendication 1 ou la revendication 2, dans lequel le traceur comprend un sel soluble dans l'eau d'au moins l'un desdits métaux.
4. Procédé selon la revendication 1 ou la revendication 2, dans lequel le traceur comprend un sel soluble dans les hydrocarbures d'au moins l'un desdits métaux.
5. Procédé selon la revendication 1 ou la revendication 2, dans lequel le traceur comprend au moins l'un desdits métaux sous forme élémentaire.
- 30      6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le traceur est sous la forme de particules finement divisées de métal ou d'un sel du métal.
7. Procédé selon la revendication 6, dans lequel les particules sont formées en une unité façonnée.
- 35      8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le réservoir est un réservoir de pétrole souterrain et/ou de gaz naturel.
9. Outil de perforation comprenant :
  - 40      - un corps allongé ayant un axe longitudinal central ;
  - un moyen de commande ;
  - un moyen de déploiement ; et
  - au moins une charge explosive montée sur ledit corps, ou à l'intérieur de celui-ci, et associée à un moyen de détonation, ladite charge étant agencée pour diriger l'énergie par explosion et vers l'extérieur depuis le corps allongé au moment de la détonation, et au moins un matériau de traceur solide monté sur ledit corps, ou à l'intérieur de celui-ci, sur la trajectoire de ladite énergie explosive,

45      **caractérisé en ce que** le matériau de traceur solide comprend au moins un métal non radioactif sélectionné dans le groupe consistant en césium, niobium, tantale, tellure, terbium, lanthane, or, iridium, osmium, argent, platine, palladium, rhénium, ruthénium, rhodium, hafnium, indium, un métal des lanthanides du tableau périodique, ou un sel dudit au moins un métal non radioactif.
10. Outil de perforation selon la revendication 9, dans lequel le traceur comprend du césium, niobium, tantale, tellure, terbium, europium, platine et rhodium ou un sel de ceux-ci.
- 55      11. Outil de perforation selon la revendication 9 ou la revendication 10, dans lequel le traceur comprend un sel soluble dans l'eau d'au moins l'un desdits métaux.

12. Outil de perforation selon la revendication 9 ou la revendication 10, dans lequel le traceur comprend un sel soluble dans les hydrocarbures d'au moins l'un desdits métaux.

5 13. Outil de perforation selon la revendication 9 ou la revendication 10, dans lequel le traceur comprend au moins l'un desdits métaux sous forme élémentaire.

10 14. Outil de perforation selon l'une quelconque des revendications 9 à 13, dans lequel l'outil comprend un manchon externe recouvrant les charges explosives et dans lequel le traceur est situé dans une ou plusieurs échancrures formées dans le manchon externe en alignement avec une ou plusieurs des charges explosives.

15 15. Outil de perforation selon l'une quelconque des revendications 9 à 13, dans lequel le traceur est situé à distance d'une charge entre ladite charge et un manchon externe dudit outil sur la trajectoire prévue du souffle de l'explosion de manière qu'au moins une partie du matériau de traceur soit transportée dans la formation de réservoir avec les gaz explosifs lors de la détonation de la charge.

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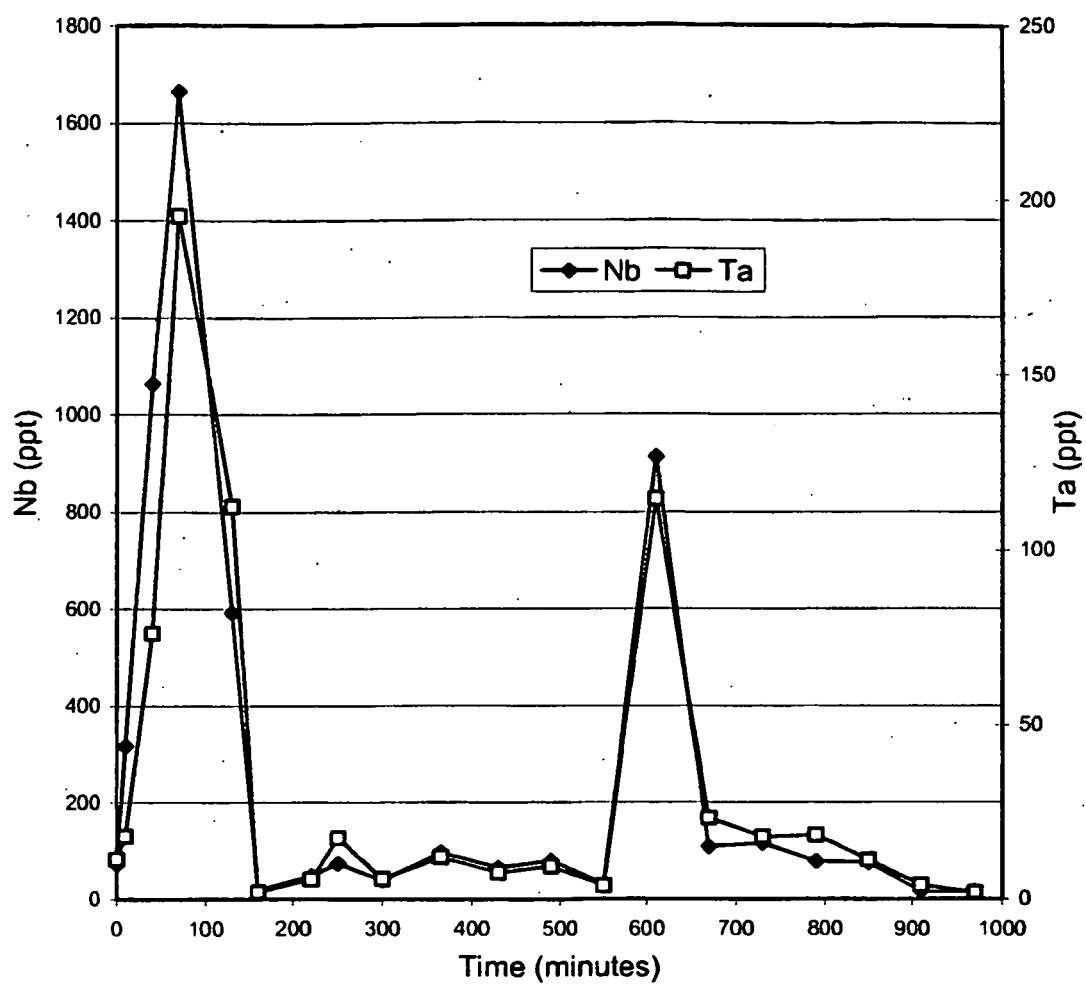
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Fig. 1



**REFERENCES CITED IN THE DESCRIPTION**

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