



(51) International Patent Classification:

*E21B 43/12* (2006.01) *G01V 9/00* (2006.01)  
*E21B 49/08* (2006.01)

(21) International Application Number:

PCT/US2015/066353

(22) International Filing Date:

17 December 2015 (17.12.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

14/601,305 21 January 2015 (21.01.2015) US

(71) Applicant: **BAKER HUGHES INCORPORATED**  
[US/US]; P.O. Box 4740, Houston, TX 77210-4740 (US).

(72) Inventors: **ZHANG, Zhihui**; 2929 Allen Parkway, Suite 2100, Houston, TX 77019-2118 (US). **DENG, Guijun**; 2929 Allen Parkway, Suite 2100, Houston, TX 77019-2118 (US). **XU, Zhiyue**; 2929 Allen Parkway, Suite 2100, Houston, TX 77019-2118 (US). **MA, Guobin**; 2929 Allen Parkway, Suite 2100, Houston, TX 77019-2118 (US). **WANG, Ke**; 2929 Allen Parkway, Suite 2100, Houston, TX 77019-2118 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

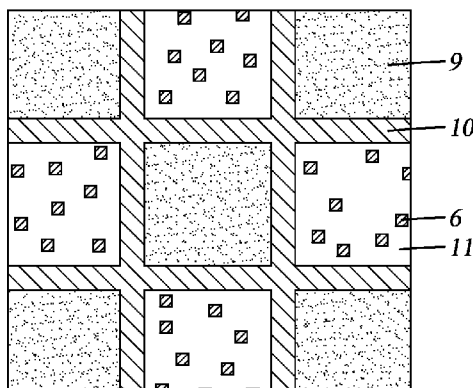
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))

(54) Title: HIGH TEMPERATURE TRACERS FOR DOWNHOLE DETECTION OF PRODUCED WATER

Fig. 1



(57) Abstract: A tracer composite comprises a tracer disposed in a metal-based carrier which comprises: a cellular nanomatrix and a metal matrix disposed in the cellular nanomatrix, wherein the tracer is detectable at a range of from about 1 ppt to about 1,000 ppm.

## HIGH TEMPERATURE TRACERS FOR DOWNHOLE DETECTION OF PRODUCED WATER

### CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Application No. 14/601305, filed on January 21, 2015, which is incorporated herein by reference in its entirety.

### BACKGROUND

[0002] In a multi-zone oil and/or gas well, monitoring when water starts producing and the flow rate of water in each zone are important to understand the dynamics of the wellbore. Tracers have been used in the past to monitor water production in reservoirs. These tracers are typically immobilized or integrated with a polymer carrier through covalent bonds or ionic interactions. Upon contact with water, the binding between the tracers and the polymer carrier breaks thus releasing the tracers. As oil and gas production activities continue to shift toward more hostile and unconventional environments, the performance of the polymer-based tracer composites may be less than desirable as the polymer carriers are susceptible to decomposition under harsh conditions. Accordingly the industry is always receptive to new tracer composites and improved methods for monitoring water production in reservoirs.

### BRIEF DESCRIPTION

[0003] The above and other deficiencies in the prior art are overcome by, in an embodiment, a tracer composite comprises a tracer disposed in a metal-based carrier which comprises: a cellular nanomatrix and a metal matrix disposed in the cellular nanomatrix, wherein the tracer is detectable at a range of from about 1 ppt to about 1,000 ppm.

[0004] An article comprising the tracer composite is also disclosed.

[0005] A method of analyzing water in a fluid produced from at least one zone of a well comprises: introducing a tracer composite into the well; obtaining a sample of the fluid produced from at least one zone of the well; and analyzing the tracer in the sample; wherein the tracer composite comprises a tracer disposed in a metal-based carrier which comprises: a cellular nanomatrix and a metal matrix disposed in the cellular nanomatrix, wherein the tracer is detectable at a range of from about 1 ppt to about 1,000 ppm.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0006] The following descriptions should not be considered limiting in any way. With reference to the accompanying drawings, like elements are numbered alike:

[0007] FIG. 1 illustrates a tracer composite according to an embodiment of the disclosure;

[0008] FIG. 2 illustrates a tracer composite wherein the tracer is uniformly dispersed in a metal-based carrier;

[0009] FIG. 3 illustrates an exemplary tracer composite comprising a core;

[0010] FIG. 4 illustrates an exemplary tracer composite comprising an outer member;

[0011] FIG. 5 illustrates a production well system for producing fluids from multiple production zones;

[0012] FIG. 6 is a schematic illustration of a sand screen protected by a perforated shroud used in the production well system of FIG. 5; and

[0013] FIG. 7 illustrates the detection of different tracers from different zones.

## DETAILED DESCRIPTION

[0014] The inventors hereof have found that the temperature rating of tracer composites can be greatly improved by incorporating tracers into disintegrable metal-based carriers. The metal-based carriers are stable in the presence of hydrocarbons but can controllably dissolve in the presence of water. Accordingly, when the tracer composites are in contact with produced water, the metal-based carriers dissolve at a controlled rate releasing the tracers as a function of the concentration of water and the environmental temperature. Compared with polymer-based carriers, metal-based carriers are much more stable thus can significantly enhance the temperature rating of the tracer composites. For example, while commercially available polymer-based tracer composites typically have a temperature rating of about 350 °F, the tracer composites of the disclosure can be used at a temperature of up to about 650 °F. In addition, when the service function of the tracer composites is complete, the metal-based carriers can completely dissolve without interfering with fluid production or other downhole operations.

[0015] Advantageously, the tracers are stable at temperatures up to about 650 °F, up to about 600 °F, up to about 550 °F or up to about 500 °F depending on the application and the specific tracers used. As a further advantageous feature, the tracers can be detected with sensitivity up to the order of part-per-trillion (ppt). In an embodiment, the tracer is detectable

at a range of from about 1 ppt to about 1,000 ppm, about 5 ppt to about 1,000 ppm, or about 50 ppt to about 500 ppm. The tracers in the tracer composites comprise one or more of the following: inorganic cations and/or inorganic anions; stable isotopes; activable elements/isotopes; or organic compounds.

[0016] The exemplary inorganic cations (also referred to as “characteristic cations”) include the cations of metals such as thorium, silver, bismuth, zirconium, chromium, copper, beryllium, cadmium, manganese, tin, rare earth metals, nickel, iron, cobalt, zinc, gallium, and the like. As used herein, rare earth metals include scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, or lutetium. In an embodiment, the metals of the characteristic cations are distinct from the metals that may be present in the formation so that it is clear that the detected characteristic cations are from the tracer composites instead of the formation.

[0017] Suitable inorganic anions (also referred to as “characteristic anions”) include complex cyanides such as dicyanoaurate complex ion  $\text{Au}(\text{CN})_2^-$ , tetracyanonickelate  $\text{Ni}(\text{CN})_4^{2-}$ ,  $\text{Co}(\text{CN})_6^{3-}$ ,  $\text{Fe}(\text{CN})_6^{3-}$ , nitrate, iodide and thiocyanate.

[0018] The characteristic anions and characteristic cations can be used independently. For example, the anions can be used in the form of salts like sodium salts and potassium salts where the corresponding cations are not characteristic cations. Alternatively, the characteristic anions and characteristic cations can be used together as the tracer materials. Liquid chromatography and ion chromatography may be applied to elute the tracers and to improve the detectability of the tracers.

[0019] Stable isotopes in nitrates, ammonium salts, sulfates, carbonates can also provide a unique signature. Exemplary isotopes include isotopes of oxygen ( $^{16}\text{O}$ ,  $^{18}\text{O}$ ), isotopes of nitrogen ( $^{14}\text{N}$ ,  $^{15}\text{N}$ ), sulfur isotopes ( $^{32}\text{S}$ ,  $^{34}\text{S}$ ,  $^{36}\text{S}$ ), carbon isotopes ( $^{12}\text{C}$ ,  $^{13}\text{C}$ ), strontium isotopes ( $^{86}\text{Sr}$ ,  $^{87}\text{Sr}$ ), hydrogen isotopes ( $^1\text{H}$ ,  $^2\text{H}$ ), boron isotopes ( $^{10}\text{B}$ ,  $^{11}\text{B}$ ), or chlorine isotopes ( $^{35}\text{Cl}$ ,  $^{37}\text{Cl}$ ).

[0020] The tracers can include activable tracers, which are nonradioactive but can be activated by neutron radiation when needed, forming new gamma-emitting tracers. Advantageously, these tracers have a very short half-life or decay very quickly. For example, the tracers can have a half-life less than about 30 days, less than about 15 days, less than about 2 days, or less than about 1 day. The activatable tracers can be diluted to reduce their level when activated. Suitable tracers include  $^{69}\text{Ga}(\text{n}, 2\text{n})^{68}\text{Ga}$ ,  $^{121}\text{Sb}(\text{n}, 2\text{n})^{120}\text{Sb}$ ,  $^{138}\text{Ba}(\text{n}, 2\text{n})^{137}\text{mBa}$ ,  $^{63}\text{Cu}(\text{n}, 2\text{n})^{62}\text{Cu}$ . Other activatable tracers having a short half-life can also be

used. The activable tracers can be activated right before sampling. For example, by selectively activating an activable tracer downhole in a particular zone or location, the information of water produced from that particular zone or location can be obtained. In this embodiment, the tracers for different zones can be the same. Alternatively, the tracer can be activated after a sample has been collected and before or when the sample is analyzed in a downstream location, for example on the ground. In this embodiment, the tracers for different zones can be different.

[0021] The tracers also include organic compounds. Certain aromatic acids and compounds can be separated and detected with high sensitivity (ppb) by ion chromatography and UV detection with significant aromatic character. Exemplary organic tracer compounds include pentafluorobenzoate; meta-trifluoromethylbenzoate; tetrafluorophthalate; 2,3-difluorobenzoic acid; 2,3-dimethylbenzoic acid; 2,4,6-trimethylbenzoic acid; 2,4-difluorobenzoic acid; 2,4-difluorophenylacetic acid; 2,4-dimethylbenzoic acid; 2,5-dimethylbenzoic acid; 2,5-dimethylbenzenesulfonic acid; 2,6-difluorobenzoic acid; 2,6-difluorophenylacetic acid; 2,6-dimethylbenzoic acid; 3,4-difluorobenzoic acid; 3,4-dimethylbenzoic acid; 3,5-dimethylbenzoic acid; 3,5-di(trifluoromethyl)benzoic acid; 3,5-di(trifluoromethyl)phenylacetic acid; 3-fluoro-4-methylbenzoic acid; 4-ethylbenzenesulfonic acid; 4-ethylbenzenesulfonic acid; 4-methylbenzenesulfonic acid; benzoic acid; benzenesulfonic acid; isophthalic acid; meta-fluorobenzoic acid; meta-fluorophenylacetic acid; meta-trifluoromethylbenzoic acid; meta-trifluoromethylphenylacetic acid; ortho-fluorobenzoic acid; ortho-trifluorophenylacetic acid; ortho-trifluoromethylbenzoic acid; ortho-trifluoromethylphenylacetic acid; phthalic acid; perfluorobenzoic acid; perfluorobenzenesulfonic acid; perfluorophenylacetic acid; para-fluorobenzoic acid; para-fluorophenylacetic acid; para-trifluoromethylbenzoic acid; para-trifluoromethylphenylacetic acid; or terephthalic acid.

[0022] Polyaromatic sulfonates have outstanding thermal stability and are stable at temperatures of up to about 650°F or up to about 570 °F. Exemplary sulfonates include 1,3,6,8-pyrene tetrasulfonate, 1,5-naphthalene disulfonate, 1,3,6-naphthalene trisulfonate, 2-naphthalene sulfonate, and 2,7-naphthalene disulfonate. Polyaromatic sulfonates can exhibit fluorescence. Their detectable concentration is in the parts per trillion (ppt) range by high performance liquid chromatography and fluorescence spectroscopy techniques.

[0023] The metal-based carriers in the tracer composites are metal composites including a cellular nanomatrix and a metal matrix disposed in the cellular nanomatrix. The cellular nanomatrix comprises a nanomatrix material. The metal matrix (e.g. a plurality of

particles) comprises a particle core material dispersed in the cellular nanomatrix. The particle core material comprises a nanostructured material. Such a metal composite having the cellular nanomatrix with metal matrix disposed therein is referred to as controlled electrolytic metallic. An exemplary metal composite and method used to make the metal composite are disclosed in U.S. Patent Application Serial Numbers 12/633,682, 12/633,688, 13/220,832, 13/220,822, and 13/358,307, the disclosure of each of which patent application is incorporated herein by reference in its entirety.

[0024] The metal matrix can include any suitable metallic particle core material that includes nanostructure as described herein. In an exemplary embodiment, the metal matrix is formed from particle cores and can include an element such as aluminum, iron, magnesium, manganese, zinc, or a combination thereof, as the nanostructured particle core material. More particularly, in an exemplary embodiment, the metal matrix and particle core material can include various Al or Mg alloys as the nanostructured particle core material, including various precipitation hardenable alloys Al or Mg alloys. More than one alloy can be present in the metal matrix. For example, the metal matrix comprises a plurality of particles wherein some of the particles are Al alloys and others are Mg alloys. In some embodiments, the particle core material includes magnesium and aluminum where the aluminum is present in an amount of about 1 weight percent (wt%) to about 15 wt%, specifically about 1 wt% to about 10 wt%, and more specifically about 1 wt% to about 5 wt%, based on the weight of the metal matrix, the balance of the weight being magnesium.

[0025] In an additional embodiment, precipitation hardenable Al or Mg alloys are particularly useful because they can strengthen the metal matrix through both nanostructuring and precipitation hardening through the incorporation of particle precipitates as described herein. The metal matrix and particle core material also can include a rare earth element, or a combination of rare earth elements. Exemplary rare earth elements include Sc, Y, La, Ce, Pr, Nd, or Er. A combination comprising at least one of the foregoing rare earth elements can be used. Where present, the rare earth element can be present in an amount of about 5 wt% or less, and specifically about 2 wt% or less, based on the weight of the metal composite.

[0026] The metal matrix and particle core material also can include a nanostructured material. In an exemplary embodiment, the nanostructured material is a material having a grain size (e.g., a subgrain or crystallite size) that is less than about 200 nanometers (nm), specifically about 10 nm to about 200 nm, and more specifically an average grain size less than about 100 nm. It will be appreciated that the nanocellular matrix and grain structure of

the metal matrix are distinct features of the metal composite. Particularly, nanocellular matrix is not part of a crystalline or amorphous portion of the metal matrix.

[0027] The cellular matrix includes aluminum, cobalt, copper, iron, magnesium, nickel, silicon, tungsten, zinc, an oxide thereof, a nitride thereof, a carbide thereof, an intermetallic compound thereof, a cermet thereof, or a combination comprising at least one of the foregoing.

[0028] The metal matrix can be present in an amount from about 50 wt% to about 95 wt%, specifically about 60 wt% to about 95 wt%, and more specifically about 70 wt% to about 95 wt%, based on the weight of the metal composite. Further, the amount of the metal nanomatrix material is about 10 wt% to about 50 wt%, specifically about 20 wt% to about 50 wt%, and more specifically about 30 wt% to about 50 wt%, based on the weight of the metal composite.

[0029] The metal composite can include a disintegration agent to control the disintegration rate of the metal composite. The disintegration agent can be disposed in the metal matrix, the cellular nanomatrix, or a combination thereof. According to an embodiment, the disintegration agent includes a metal, fatty acid, ceramic particle, or a combination comprising at least one of the foregoing, the disintegration agent being disposed among the controlled electrolytic material to change the disintegration rate of the controlled electrolytic material. In one embodiment, the disintegration agent is disposed in the cellular nanomatrix external to the metal matrix. In a non-limiting embodiment, the disintegration agent increases the disintegration rate of the metal composite. In another embodiment, the disintegration agent decreases the disintegration rate of the metal composite. The disintegration agent can be a metal including cobalt, copper, iron, nickel, tungsten, zinc, or a combination comprising at least one of the foregoing. In a further embodiment, the disintegration agent is the fatty acid, e.g., fatty acids having 6 to 40 carbon atoms. Exemplary fatty acids include oleic acid, stearic acid, lauric acid, hydroxystearic acid, behenic acid, arachidonic acid, linoleic acid, linolenic acid, ricinoleic acid, palmitic acid, montanic acid, or a combination comprising at least one of the foregoing. In yet another embodiment, the disintegration agent is ceramic particles such as boron nitride, tungsten carbide, tantalum carbide, titanium carbide, niobium carbide, zirconium carbide, boron carbide, hafnium carbide, silicon carbide, niobium boron carbide, aluminum nitride, titanium nitride, zirconium nitride, tantalum nitride, or a combination comprising at least one of the foregoing. Additionally, the ceramic particle can be one of the ceramic materials discussed below with regard to the strengthening agent. Such ceramic particles have a size of 5  $\mu\text{m}$  or less,

specifically 2  $\mu\text{m}$  or less, and more specifically 1  $\mu\text{m}$  or less. The disintegration agent can be present in an amount effective to cause disintegration of the metal composite 200 at a desired disintegration rate, specifically about 0.25 wt% to about 15 wt%, specifically about 0.25 wt% to about 10 wt%, specifically about 0.25 wt% to about 1 wt%, based on the weight of the metal composite.

[0030] In metal composite, the metal matrix dispersed throughout the cellular nanomatrix can have an equiaxed structure in a substantially continuous cellular nanomatrix or can be substantially elongated along an axis so that individual particles of the metal matrix are oblatelly or prolately shaped, for example. In the case where the metal matrix has substantially elongated particles, the metal matrix and the cellular nanomatrix may be continuous or discontinuous. The size of the particles that make up the metal matrix can be from about 50 nm to about 800  $\mu\text{m}$ , specifically about 500 nm to about 600  $\mu\text{m}$ , and more specifically about 1  $\mu\text{m}$  to about 500  $\mu\text{m}$ . The particle size of can be monodisperse or polydisperse, and the particle size distribution can be unimodal or bimodal. Size here refers to the largest linear dimension of a particle.

[0031] In an embodiment, the metal composite has a metal matrix that includes particles having a particle core material. Additionally, each particle of the metal matrix is disposed in a cellular nanomatrix which is a network that substantially surrounds the component particles of the metal matrix.

[0032] As used herein, the term cellular nanomatrix does not connote the major constituent of the powder compact, but rather refers to the minority constituent or constituents, whether by weight or by volume. This is distinguished from most matrix composite materials where the matrix comprises the majority constituent by weight or volume. The use of the term substantially continuous, cellular nanomatrix is intended to describe the extensive, regular, continuous and interconnected nature of the distribution of nanomatrix material within the metal composite. As used herein, “substantially continuous” describes the extension of the nanomatrix material throughout the metal composite such that it extends between and envelopes substantially all of the metal matrix. Substantially continuous is used to indicate that complete continuity and regular order of the cellular nanomatrix around individual particles of the metal matrix are not required. For example, defects in the coating layer over particle core on some powder particles may cause bridging of the particle cores during sintering of the metal composite, thereby causing localized discontinuities to result within the cellular nanomatrix, even though in the other portions of the powder compact the cellular nanomatrix is substantially continuous and exhibits the

structure described herein. In contrast, in the case of substantially elongated particles of the metal matrix (i.e., non-equiaxed shapes), such as those formed by extrusion, “substantially discontinuous” is used to indicate that incomplete continuity and disruption (e.g., cracking or separation) of the nanomatrix around each particle of the metal matrix, such as may occur in a predetermined extrusion direction. As used herein, “cellular” is used to indicate that the nanomatrix defines a network of generally repeating, interconnected, compartments or cells of nanomatrix material that encompass and also interconnect the metal matrix. As used herein, “nanomatrix” is used to describe the size or scale of the matrix, particularly the thickness of the matrix between adjacent particles of the metal matrix. The metallic coating layers that are sintered together to form the nanomatrix are themselves nanoscale thickness coating layers. Since the cellular nanomatrix at most locations, other than the intersection of more than two particles of the metal matrix, generally comprises the interdiffusion and bonding of two coating layers from adjacent powder particles having nanoscale thicknesses, the cellular nanomatrix formed also has a nanoscale thickness (e.g., approximately two times the coating layer thickness as described herein) and is thus described as a nanomatrix. The thickness of the nanomatrix can be tuned during heat treatment by adjusting the temperature and the duration that the coated powder particles are heated. In an embodiment, the nanomatrix has a thickness of about 10 nm to about 200  $\mu\text{m}$ , or about 1  $\mu\text{m}$  to about 50  $\mu\text{m}$ . Further, the use of the term metal matrix does not connote the minor constituent of metal composite, but rather refers to the majority constituent or constituents, whether by weight or by volume. The use of the term metal matrix is intended to convey the discontinuous and discrete distribution of particle core material within metal composite.

[0033] The tracers are present in an amount of about 1 to about 70 vol.%, about 2 to about 60 vol.%, or about 5 vol. to about 50 vol.% based on the total volume of the tracer composites. Traces can be uniformly dispersed in the tracer composites. The tracer can be dispersed in the metal matrix, the cellular nanomatrix, or both. As used herein, “dispersed” means that the tracer is blended with the carrier on a micrometer size level and “dispersed” does not include doping such as adding a tracer in the atomic size level where the tracer is on the lattice sites of the carrier.

[0034] In an embodiment, the tracer composites further comprise a disintegrable core. In another embodiment, the tracer composites further comprise an outer member disposed on a surface of the tracer composites. The outer member has a plurality of apertures to allow produced fluids to contact the metal-based carrier. It is appreciated that the tracer composites can include both a core and an outer member.

[0035] The core and the outer member can independently comprise one or more of the following: a disintegrable metal; a disintegrable metal alloy; or a disintegrable metal composite as disclosed herein. Exemplary materials for the tracer composite core include those consolidated or forged from coated particles having a core comprising Mg metal or an Mg alloy such as Mg-Si, Mg-Al, Mg-Zn, Mg-Mn, Mg-Al-Zn, Mg-Al-Mn, Mg-Zn-Zr, or Mg-rare earth alloys, and a coating comprising one or more of the following: Al; Ni; Fe; W; Cu; or Co. Exemplary materials for the tracer composite core also include Al, Zn, or Mn, alloyed with one or more of the following: Al; Mg; Mn; Zn; Cu; In; Ga; Si; Sn; or Pb. The materials for the outer member include those materials for the tracer composite core as well as non-degradable materials. In an embodiment, the outer member of the tracer composites comprises steel. In an embodiment, the core and the outer member have a slower disintegrating rate than the metal-based carrier (metal composite) when tested at the same testing conditions. Alternatively, the core or the outer member can be formed from materials that are not disintegrable in downhole environments.

[0036] The materials for the core and the outer member can be stronger than the material for the metal-based carrier. Thus by including a core or an outer member, the structural integrity of the tracer composites can be maintained.

[0037] Exemplary embodiments of the tracer composites are shown in FIGs 1-4. Referring to FIG. 1, the tracer composite comprises cellular nanomatrix 10 and metal matrixes 9 and 11. The metal matrixes 9 and 11 can be the same or different. In some embodiments, metal matrix 9 includes magnesium alloys, metal matrix 11 includes aluminum alloys, and the cellular nanomatrix 10 includes Ni, Fe, Cu, W, Co, and the like. Although it is shown in FIG. 1 that the tracer 6 is disposed only in metal matrix 11, it is appreciated that the tracer can be disposed in matrix 9, the cellular nanomatrix 10, or both.

[0038] FIG. 2 shows that tracer 6 is uniformly distributed in a metal-based carrier 5. Referring to FIG. 3, the tracer composite further includes a disintegrable core 7. Referring to FIG. 4, the tracer composite can further include an outer member 8.

[0039] The tracer composites can be formed from a combination of, for example, tracers and powder constituents. The powder constituents include coated particles or a combination of coated particles and uncoated particles. The method includes compacting, sintering, forging such as by cold isostatic pressing (CIP), hot isostatic pressing (HIP), or dynamic forging. The cellular nanomatrix and nanomatrix material are formed from metallic coatings on the coated particles. The chemical composition of nanomatrix material may be different than that of coating material due to diffusion effects associated with the sintering.

The metal-based carrier (metal composite) also includes a plurality of particles that make up the metal matrix that comprises the particle core material. The metal matrix and particle core material correspond to and are formed from the plurality of particle cores and core material of the plurality of powder particles as the metallic coating layers are sintered together to form the cellular nanomatrix. The chemical composition of particle core material may also be different than that of core material due to diffusion effects associated with sintering.

[0040] A method of analyzing water in a fluid produced from at least one zone of a well includes: introducing a tracer composite into the well; obtaining a sample of the fluid produced from at least one zone of the well; and analyzing the tracer in the sample.

[0041] The tracer composites can be incorporated into various downhole articles. As an example, a metallic tracer rod 2 made of the tracer composite disclosed herein is installed between sandscreen 3 and protecting shroud 4 as shown in FIG. 6. The sandscreen assembly 1 can be installed in a production well system for producing fluids from multiple production zones as shown in FIG. 5.

[0042] In an embodiment, the tracer composites are used in a well having multiple production zones. The tracer composites used can be unique for each zones. For example, tracers in the trace composites disposed in each zone have different chemical structures. Based on the amount of measured tracers the amount of water flowing into the well at each zone can be calculated. As illustrated in FIG. 7, the concentrations of tracers 1, 2, and 3 indicate the water production levels at zones 1, 2, and 3. In another embodiment, the tracers for different zones are the same. When the water production information in a particular zone is needed, the tracer in the trace composite of that zone can be selectively activated thus providing information of water production in that zone.

[0043] Once a sample has been obtained, analysis for the presence and concentrations of the selected tracers may be carried out. Suitable instruments include, but are not limited to, gas chromatography (GC) using flame ionization detectors, electron capture detectors, and the like; liquid chromatography (LC), infrared (IR) spectroscopy; mass spectroscopy (MS); combination instrumentation such as Fourier transform infrared (FTIR) spectroscopy, GC-MS, LC-MS, and the like. The tracer may be detectable at a range of from about 1 ppt to about 1,000 ppm, about 5 ppt to about 1,000 ppm, or about 50 ppt to about 500 ppm. Once the tracer concentration has been determined, the information may be used in a variety of ways. For example, the concentration of detected tracers can provide information of the flow rate of produced water. Downhole water production detection and quantitative analysis method disclosed herein can be used for single zone or multiple zones for conventional oil

and gas, deepwater, unconventional oil and gas, and stream-assisted gravity drainage applications.

[0044] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other. “Or” means “and/or.” “Optional” or “optionally” means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event occurs and instances where it does not. As used herein, “combination” is inclusive of blends, mixtures, alloys, reaction products, and the like. “A combination thereof” means “a combination comprising one or more of the listed items and optionally a like item not listed.” All references are incorporated herein by reference.

[0045] The use of the terms “a” and “an” and “the” and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Further, it should further be noted that the terms “first,” “second,” and the like herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another. The modifier “about” used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., it includes the degree of error associated with measurement of the particular quantity).

[0046] While typical embodiments have been set forth for the purpose of illustration, the foregoing descriptions should not be deemed to be a limitation on the scope herein. Accordingly, various modifications, adaptations, and alternatives can occur to one skilled in the art without departing from the spirit and scope herein.

## CLAIMS

What is claimed is:

1. A tracer composite (9, 10, 11) comprising a tracer (6) disposed in a metal-based carrier (5) which comprises:
  - a cellular nanomatrix (10); and
  - a metal matrix (9, 11) disposed in the cellular nanomatrix (10),
 wherein the tracer (6) is detectable at a range of from about 1 ppt to about 1,000 ppm.
2. The tracer composite (9, 10, 11) of claim 1, wherein the tracer (6) is present in an amount of 1 to 70 vol.% based on the total volume of the tracer composite (9, 10, 11).
3. The tracer composite (9, 10, 11) of claim 1 or claim 2, wherein the tracer (6) composite further comprises a disintegrable core (7), wherein the disintegrable core (7) has a slower disintegrating rate than the metal-based carrier (5) when measured at the same testing conditions.
4. The tracer composite (9, 10, 11) of any one of claims 1 to 3, wherein the tracer (6) composite further comprises an outer member (8) disposed on a surface of the tracer composite (9, 10, 11), optionally the outer member (8) has a plurality of apertures.
5. The tracer composite (9, 10, 11) of claim 4, wherein the outer member (8) comprises one or more of the following: a disintegrable metal; a disintegrable metal alloy; a disintegrable metal composite; or a non-degradable material; and wherein the outer member (8) has a slower disintegrating rate than the metal-based carrier (5) when tested at the same testing conditions.
6. The tracer composite (9, 10, 11) of any one of claims 1 to 5, wherein the metal matrix (9, 11) comprises magnesium; and the cellular nanomatrix (10) comprises aluminum, calcium, cobalt, copper, iron, magnesium, molybdenum, nickel, silicon, zinc, an intermetallic compound thereof, or a combination thereof.
7. The tracer composite (9, 10, 11) of any one of claims 1 to 6, wherein the metal-based carrier (5) further comprises a disintegration agent comprising one or more of the following: cobalt; copper; iron; or nickel.
8. The tracer composite (9, 10, 11) of any one of claims 1 to 7, wherein the tracer (9, 10, 11) comprises one or more of the following: an inorganic cation; an inorganic anion; an isotope; an activatable element; or an organic compound;
 

the inorganic anion comprises one or more of the following:  $\text{Au}(\text{CN})_2^{2-}$ ;  $\text{Ni}(\text{CN})_4^{2-}$ ;  $\text{Co}(\text{CN})_6^{3-}$ ;  $\text{Fe}(\text{CN})_6^{3-}$ ;  $\text{NO}_3^-$ ;  $\text{I}^-$ ; or  $\text{SCN}^-$ ;

the inorganic cation comprises the cation of one or more of the following metals: thorium; silver; bismuth; zirconium; chromium; copper; beryllium; cadmium; manganese; tin; rare earth metals; nickel; iron; cobalt; zinc; or gallium;

the isotope comprises one or more of the following:  $^{16}\text{O}$ ;  $^{18}\text{O}$ ;  $^{14}\text{N}$ ;  $^{15}\text{N}$ ;  $^{32}\text{S}$ ;  $^{34}\text{S}$ ;  $^{36}\text{S}$ ;  $^{12}\text{C}$ ;  $^{13}\text{C}$ ;  $^{86}\text{Sr}$ ;  $^{87}\text{Sr}$ ;  $^1\text{H}$ ;  $^2\text{H}$ ;  $^{10}\text{B}$ ;  $^{11}\text{B}$ ;  $^{35}\text{Cl}$ , or  $^{37}\text{Cl}$ ;

the activatable element comprises one or more of the following:  $^{69}\text{Ga}(\text{n}, 2\text{n})^{68}\text{Ga}$ ,  $^{121}\text{Sb}(\text{n}, 2\text{n})^{120}\text{Sb}$ ,  $^{138}\text{Ba}(\text{n}, 2\text{n})^{137}\text{mBa}$ , or  $^{63}\text{Cu}(\text{n}, 2\text{n})^{62}\text{Cu}$ ; and

the organic compound comprises one or more of the following: pentafluorobenzoate; meta-trifluoromethylbenzoate; tetrafluorophthalate; 2,3-difluorobenzoic acid; 2,3-dimethylbenzoic acid; 2,4,6-trimethylbenzoic acid; 2,4-difluorobenzoic acid; 2,4-difluorophenylacetic acid; 2,4-dimethylbenzoic acid; 2,5-dimethylbenzoic acid; 2,5-dimethylbenzenesulfonic acid; 2,6-difluorobenzoic acid; 2,6-difluorophenylacetic acid; 2,6-dimethylbenzoic acid; 3,4-difluorobenzoic acid; 3,4-dimethylbenzoic acid; 3,5-dimethylbenzoic acid; 3,5-di(trifluoromethyl)benzoic acid; 3,5-di(trifluoromethyl)phenylacetic acid; 3-fluoro-4-methylbenzoic acid; 4-ethylbenzenesulfonic acid; 4-ethylbenzenesulfonic acid; 4-methylbenzenesulfonic acid; benzoic acid; benzenesulfonic acid; isophthalic acid; meta-fluorobenzoic acid; meta-fluorophenylacetic acid; meta-trifluoromethylbenzoic acid; meta-trifluoromethylphenylacetic acid; ortho-fluorobenzoic acid; ortho-trifluorophenylacetic acid; ortho-trifluoromethylbenzoic acid; ortho-trifluoromethylphenylacetic acid; phthalic acid; perfluorobenzoic acid; perfluorobenzenesulfonic acid; perfluorophenylacetic acid; para-fluorobenzoic acid; para-fluorophenylacetic acid; para-trifluoromethylbenzoic acid; para-trifluoromethylphenylacetic acid; terephthalic acid; 1,3,6,8-pyrene tetrasulfonate; 1,5-naphthalene disulfonate; 1,3,6-naphthalene trisulfonate; 2-naphthalene sulfonate; or 2,7-naphthalene disulfonate.

9. An article comprising the tracer composite (9, 10, 11) of any one of claims 1-8.

10. A method of analyzing water in a fluid produced from at least one zone of a well, the method comprising:

introducing a tracer composite (9, 10, 11) into the well;

obtaining a sample of the fluid produced from at least one zone of the well; and

analyzing the tracer (6) in the sample;

wherein the tracer composite (9, 10, 11) comprises a tracer (6) disposed in a metal-based carrier (5) which comprises: a cellular nanomatrix (10) and a metal matrix (9, 11)

disposed in the cellular nanomatrix (10), wherein the tracer (6) is detectable at a range of from about 1 ppt to about 1,000 ppm.

11. The method of claim 10, wherein analyzing the tracer (6) comprises determining the concentration of the tracer (6) using one or more of the following: gas chromatography (GC); liquid chromatography (LC); infrared spectroscopy (IR); mass spectroscopy (MS); Fourier transform infrared spectroscopy (FT-IR); GC-MS; or LC-MS.

12. The method of claim 10 or claim 11, wherein the tracer (6) composite is included in a downhole article.

13. The method of any one of claims 10 to 12, wherein separate tracer composites (0, 10, 11) are included in separate downhole articles located at different zones of the well.

14. The method of any one of claims 10 to 13, wherein the method further comprises determining the flow rate of water in the produced fluid.

15. The method of claim 13 or claim 14, wherein the method further comprises selectively activate the tracer (6) of the tracer composite (9, 10, 11) disposed at a first zone of the well to analyze water in a fluid produced from the first zone.

1/4

Fig. 1

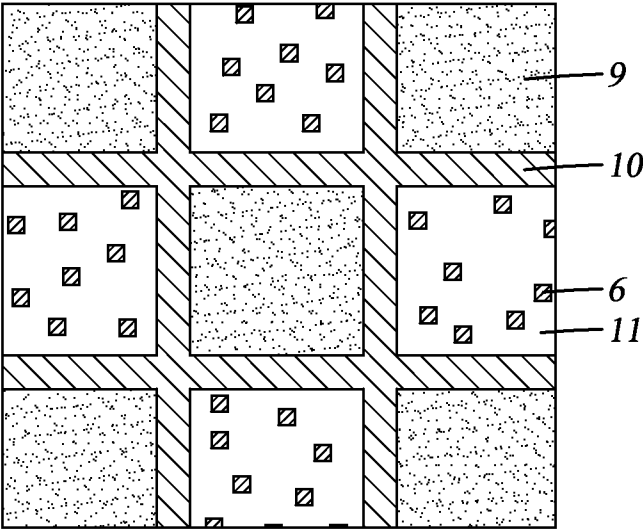


Fig. 2

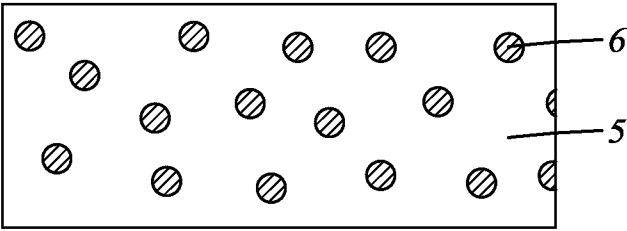


Fig. 3

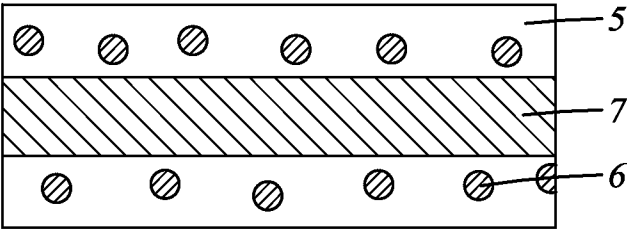


Fig. 4

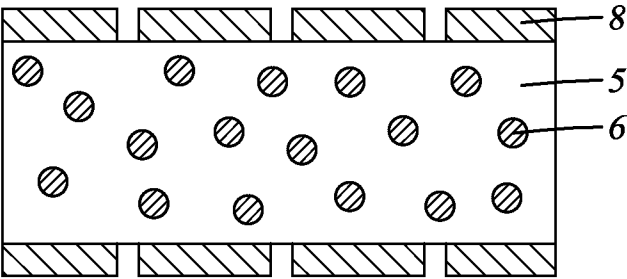
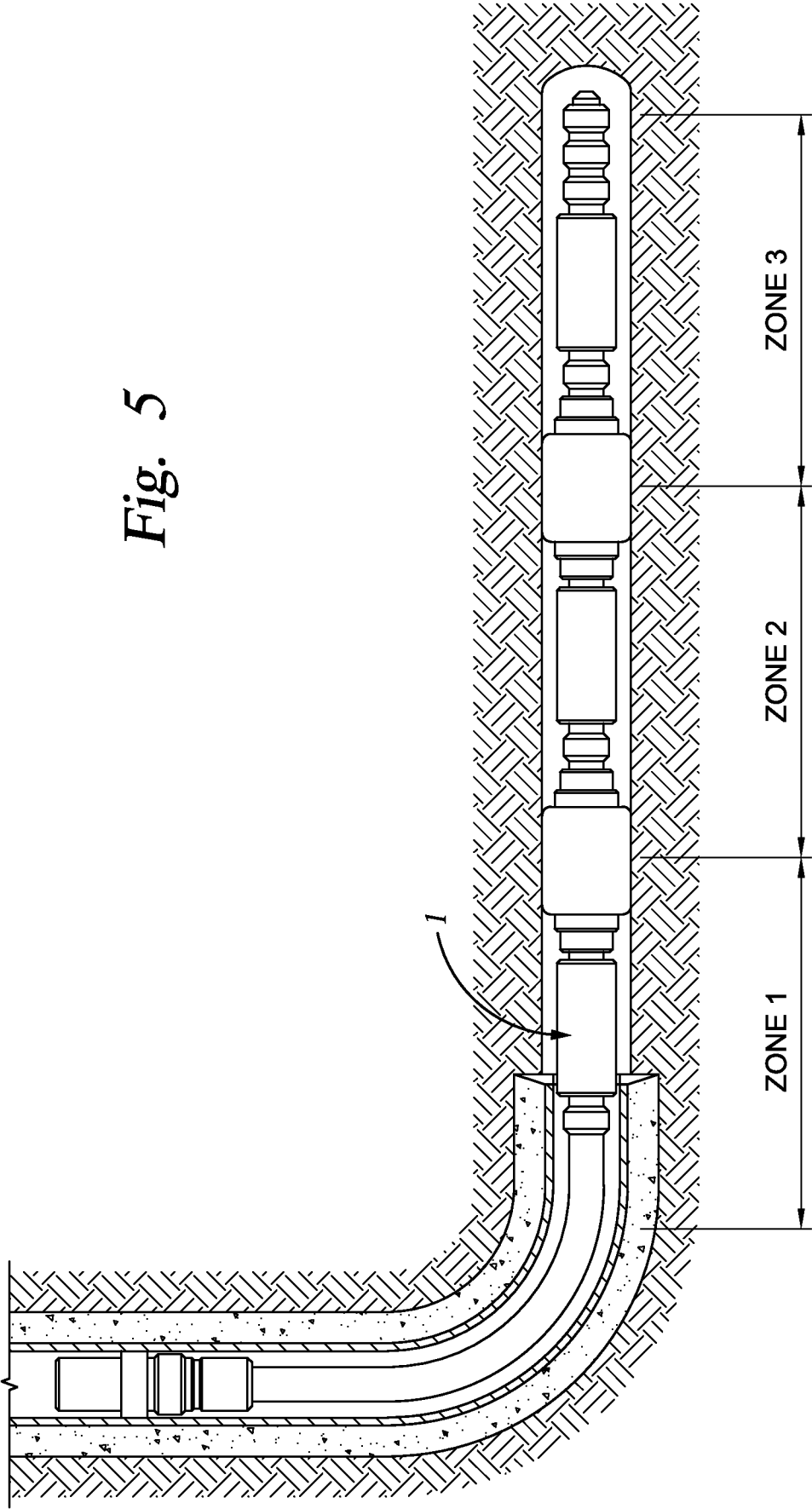


Fig. 5



3/4

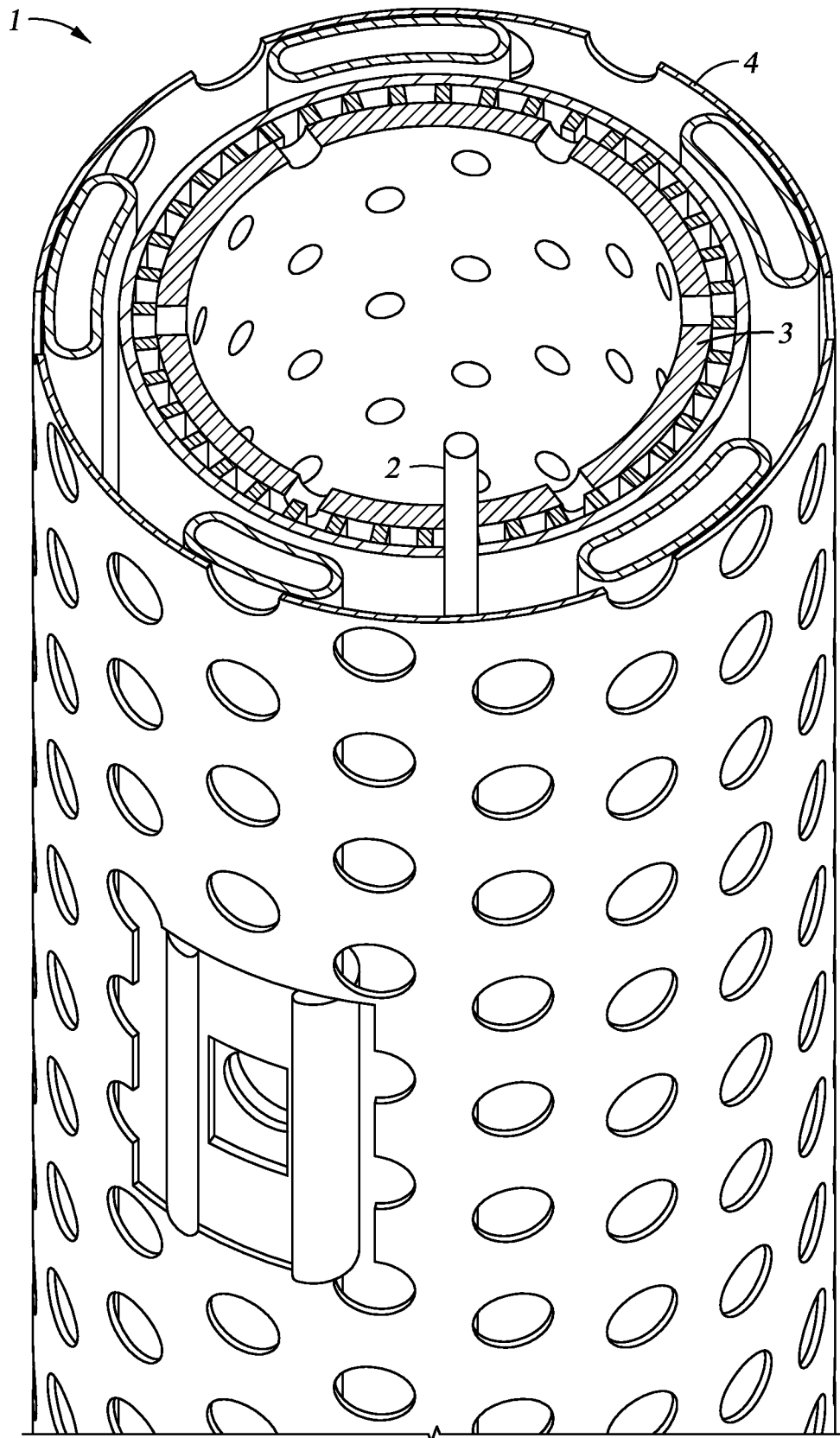
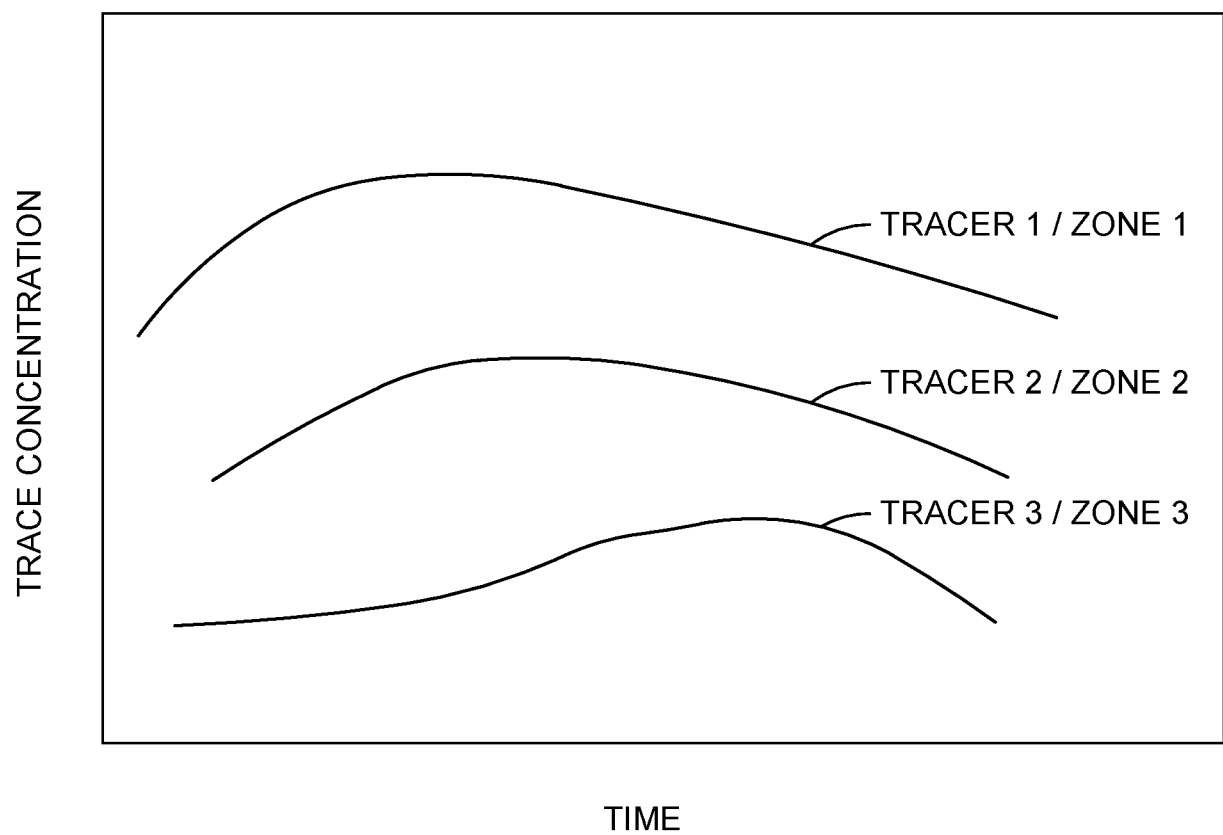


Fig. 6

4/4

*Fig. 7*

## INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/US2015/066353****A. CLASSIFICATION OF SUBJECT MATTER****E21B 43/12(2006.01)i, E21B 49/08(2006.01)i, G01V 9/00(2006.01)i**

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)

E21B 43/12; E21B 47/00; G01V 9/02; E21B 43/00; E21B 49/00; G01N 21/64; G01F 1/704; E21B 49/08; G01V 9/00

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) &amp; Keywords: composite, tracer, metal, carrier, matrix, concentration, analyzing, and sample

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                          | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| Y         | US 2002-0020527 A1 (KILAAS et al.) 21 February 2002<br>See paragraphs [0005], [0031], [0040], [0043], [0060], [0064]; claims 15, 23; and figures 3, 6-7, 9. | 1-3, 10-12            |
| Y         | US 2010-0314105 A1 (ROSE, PETER E.) 16 December 2010<br>See paragraphs [0020], [0043]; claims 1, 5, 14; and figure 1.                                       | 1-3, 10-12            |
| A         | US 2005-0235757 A1 (DE JONGE et al.) 27 October 2005<br>See paragraphs [0083]-[0084]; claim 12; and figures 1-3, 5.                                         | 1-3, 10-12            |
| A         | US 2013-0084643 A1 (COMMARIEU et al.) 04 April 2013<br>See paragraphs [0005], [0011], [0054]; claim 1; and figure 1.                                        | 1-3, 10-12            |
| A         | US 6401547 B1 (HATFIELD et al.) 11 June 2002<br>See claim 1 and figures 1A-3.                                                                               | 1-3, 10-12            |



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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

25 March 2016 (25.03.2016)

Date of mailing of the international search report

**01 April 2016 (01.04.2016)**

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

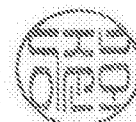
189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea

Facsimile No. +82-42-481-8578

Authorized officer

RHEE, Jun Ho

Telephone No. +82-42-481-8288



**INTERNATIONAL SEARCH REPORT**International application No.  
**PCT/US2015/066353****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.: 5  
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:  
Claim 5 is unclear because it is dependent on multiple dependent claim 4 which does not comply with PCT Rule 6.4(a).
3. ☒ Claims Nos.: 4, 6-9, 13-15  
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:

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 any 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.:

**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.

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/US2015/066353**

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|---------------------|----------------------------|---------------------|
| US 2002-0020527 A1                        | 21/02/2002          | AT 293205 T                | 15/04/2005          |
|                                           |                     | BR 0112621 A               | 10/06/2003          |
|                                           |                     | BR 0112621 B1              | 23/02/2010          |
|                                           |                     | CA 2416645 A1              | 31/01/2002          |
|                                           |                     | CA 2416645 C               | 04/05/2010          |
|                                           |                     | DE 60110081 D1             | 19/05/2005          |
|                                           |                     | DK 1301686 T3              | 15/08/2005          |
|                                           |                     | EA 004357 B1               | 29/04/2004          |
|                                           |                     | EP 1301686 A2              | 16/04/2003          |
|                                           |                     | EP 1301686 B1              | 13/04/2005          |
|                                           |                     | MX PA03000534 A            | 10/09/2004          |
|                                           |                     | US 6672385 B2              | 06/01/2004          |
|                                           |                     | WO 02-08562 A2             | 31/01/2002          |
|                                           |                     | WO 02-08562 A3             | 04/04/2002          |
| US 2010-0314105 A1                        | 16/12/2010          | AU 2010-259936 A1          | 02/02/2012          |
|                                           |                     | EP 2440744 A1              | 18/04/2012          |
|                                           |                     | US 8162049 B2              | 24/04/2012          |
|                                           |                     | WO 2010-144872 A1          | 16/12/2010          |
| US 2005-0235757 A1                        | 27/10/2005          | AU 2003-230081 A1          | 02/12/2003          |
|                                           |                     | CA 2485998 A1              | 27/11/2003          |
|                                           |                     | CA 2485998 C               | 05/07/2011          |
|                                           |                     | EP 1527326 A1              | 04/05/2005          |
|                                           |                     | JP 04330526 B2             | 16/09/2009          |
|                                           |                     | JP 2005-525569 A           | 25/08/2005          |
|                                           |                     | US 7325443 B2              | 05/02/2008          |
| US 2013-0084643 A1                        | 04/04/2013          | WO 03-098167 A1            | 27/11/2003          |
|                                           |                     | AR 079702 A1               | 15/02/2012          |
|                                           |                     | CA 2784763 A1              | 30/06/2011          |
|                                           |                     | FR 2954796 A1              | 01/07/2011          |
|                                           |                     | GB 2489363 A               | 26/09/2012          |
|                                           |                     | NO 20120680 A              | 04/09/2012          |
| US 6401547 B1                             | 11/06/2002          | WO 2011-076874 A1          | 30/06/2011          |
|                                           |                     | AT 398278 T                | 15/07/2008          |
|                                           |                     | AU 2001-12083 A1           | 14/05/2001          |
|                                           |                     | AU 2001-12083 B2           | 22/07/2004          |
|                                           |                     | CA 2389112 A1              | 10/05/2001          |
|                                           |                     | CA 2389112 C               | 23/01/2007          |
|                                           |                     | DE 60039179 D1             | 24/07/2008          |
|                                           |                     | EP 1224438 A1              | 24/07/2002          |
|                                           |                     | EP 1224438 B1              | 11/06/2008          |
|                                           |                     | JP 2003-513263 A           | 08/04/2003          |
|                                           |                     | WO 01-33173 A1             | 10/05/2001          |