US 20130341012A1

(19) United States

(12) Patent Application Publication

(10) Pub. No.: US 2013/0341012 A1

(43) Pub. Date: Dec. 26, 2013

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(54) METHOD FOR TRACKING A TREATMENT FLUID IN A SUBTERRANEAN FORMATION

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(21) Appl. No.: **13/977,538**

(22) PCT Filed: **Dec. 30, 2010**

(86) PCT No.: **PCT/RU10/00803**

§ 371 (c)(1),
(2), (4) Date: **Sep. 13, 2013**

Publication Classification

(51) **Int. Cl.**
E21B 47/10 (2006.01)

(52) **U.S. Cl.**
CPC ***E21B 47/10*** (2013.01)
USPC **166/250.12**

(57) **ABSTRACT**

A method of tracking a treatment fluid in a subterranean formation penetrated by a wellbore provides for injecting the treatment fluid with the plurality of tracer agents into the well and the formation. Each tracer agent is an object of submicron scale. The location and distribution of the treatment fluid is determined by detecting changes in the physical properties of the formation caused by the arrival of the treatment fluid comprising a plurality of tracer agents.

METHOD FOR TRACKING A TREATMENT FLUID IN A SUBTERRANEAN FORMATION

FIELD OF THE INVENTION

[0001] This invention relates generally to the recovery of hydrocarbons from a subterranean formation penetrated by a well bore and more particularly to non-radioactive tracers and methods of utilizing the non-radioactive tracers for tracking treatment and reservoir fluids in the formation in order to evaluate and understand the operations executed in the wellbore and/or in the reservoir, near wellbore and wellbore processes and fluid placements such as gravelling packing, hydraulic fracturing, sand control and cementing and drilling fluids flow and placement.

BACKGROUND OF INVENTION

[0002] The use of various kinds of markers/tracers in the oil and gas industry is well known. Radioactive and/or chemical tracers which can be readily identified are used for monitoring of treatment fluids injection into the reservoir as a means to monitor hydraulic fracturing, acidizing, water control and other wellbore and reservoir treatments.

[0003] Thus, U.S. Pat. No. 5,243,190 provides an example of radioactive elements incorporated within ceramic particles and used for tracing flow of proppant particles employed in the process of hydraulic fracturing of wells. The use of radioactive or chemical substances as tracers sometimes is not desirable and is even prohibited by environmental regulations.

[0004] Other techniques using non-radioactive tracers have also been proposed. U.S. Pat. No. 6,725,926 proposes the use of tracer agents selected from the group consisting of water soluble inorganic salts, water soluble organic salts, metals, metal salts of organic acids, metal oxides, metal sulfates, metal phosphates, metal carbonates, metal salts, phosphorescent pigments, fluorescent pigments, photoluminescent pigments etc.

[0005] Inexpensive tracers and analysis, with a short reservoir lifetime of a week or so, thiocyanate, bromide, iodide or nitrate salts can be used (Hutchins, R. D. et al., Aqueous Tracers for Oilfield Applications, SPE International Symposium on Oilfield Chemistry, 20-22 Feb. 1991, Anaheim, Calif., 21049-MS).

[0006] Analysis can be done with ion or liquid chromatography, which is lab based and expensive, but qualitative tests using "Spot Plate Tests" are available to detect nitrate, thiocyanate and iodide to roughly gauge the level by color intensity as simple and even on-site usage solution. Alternatively Iodide and thiocyanate salts have simple spectrometer tests that can be used instead chromatography for quantitative analysis. These ions should not interfere with the typical fluid crosslinking chemistry used in hydraulic fracturing, as they are used at levels of 1000 ppm or so and detectable to 1 ppm. The sodium, ammonium or potassium salts are soluble and have been used in tracing of fluid movements in the reservoir.

[0007] Chemical tracers with the explanation of their use and the methodology of measurements in post frac and long term flowback analysis are published in Mahmoud Asadi et al., Comparative Study of Flowback Analysis Using Polymer Concentrations and Fracturing Fluid Tracer Methods: A Field Study, International Oil & Gas Conference and Exhibition in China, 5-7 Dec. 2006, Beijing, China, SPE 101614, and Mahmoud Asadi et al., Post-Frac Analysis Based on Flowback Results Using Chemical Frac-Tracers, International Petroleum Technology Conference, 3-5 Dec. 2008, Kuala Lumpur, Malaysia, IPTC 11891.

[0008] Fluorescent markers and tracers can be made for Water Based fluids and are used in concentration of 0.018 ml in 180 ml filtrate and fluorescent markers and tracers for Synthetic/Oil Based fluids (concentration from 9 to 36 microliters in 180 ml filtrate).

[0009] Though these methods are quite useful there is a need for an environmentally friendly high resolution method for tracking treatment fluids that are capable of entering the drilling mud cake, gravel pack, proppant pack and other large porous media and also capable of entering without plugging the pore throats into the pore space (or fractures and fissures) of the reservoir to a reasonable distance.

SUMMARY OF INVENTION

[0010] It is therefore an object of the invention to provide a method for tracking a treatment fluid in a subterranean formation penetrated by a wellbore comprising the steps of providing the treatment fluid comprising a plurality of tracer agents, wherein each tracer agent is an object of submicron scale, injecting the treatment fluid with the plurality of tracer agents into the wellbore and the formation, and determining the location and distribution of the treatment fluid by detecting changes in the physical properties of the formation caused by the arrival of treatment fluid comprising a plurality of tracer agents.

[0011] The treatment fluid is selected from the group consisting of fracturing fluids, drilling fluids, acidizing fluids, injection fluids, brines and completion fluids, fluids for EOR/IOR including reservoir flooding fluids.

[0012] According to one embodiment, the plurality of tracer agents are low or insoluble gas bubbles having a diameter of not more than 500 nm and the treatment fluid with the plurality of tracer agents is a highly dispersed gas-liquid mixture. Suitable gases for use as the tracer agents are methane, higher molecular weight hydrocarbon gas, nitrogen or other insoluble inorganic gas or mixtures of thereof.

[0013] The nano-bubbles are normally created by dispersion of above mentioned gas or gases in water- or hydrocarbon-based solutions Water solutions can be made with different conventional oilfield salts (NaCl, KCl, $CaCl_2$, $ZnBr_2$, $CaBr_2$, and other inorganic or organic brines and their mixtures) that are used as completions solutions (brines and heavy brines) and other oilfield fluids. Nano-bubbles can be particularly strongly stabilized with electrolytes of ferrous ions, manganese ions, calcium ions, or any other mineral ion is added to the aqueous solution such that the electrical conductivity in the aqueous solution becomes not less than 300 μS/cm. The nano-bubble is a very tiny bubble having a diameter of not more than 500 nm, so that the nano-bubble does not experience buoyant forces and rupture near the fluid surface, which is observed in normal and micro-bubbles.

[0014] According to another embodiment, the plurality of tracer agents are high viscous liquid droplets having a diameter of not more than 1000 nm and the treatment fluid with the plurality of tracer agents is an emulsion such as crude oil in water, toluene in water etc. where water is fresh water, solutions of different salts (inorganic as NaCl, KCl, NH_4Cl, $CaCl_2$, $MgCl_2$, $NaBr_2$, $ZnBr_2$, $CaBr_2$, or of organic nature such as sodium formate, potassium formate and other brines and their mixtures commonly used in stimulation, gravel pack and completion operations including) in water (saturated or under-saturated), brines and water with other chemicals such as surfactants, biocides, clay control, iron control, scale control etc. used as additives. It is not unusual that the emulsions are stabilized with the use of nano-solid particles, such as silica, for example. Size of the silica nano-particles ranges between 2-500 nm, The loading of the solid nano-particles for the purpose of the stabilization has seen concentrations from 0.1 wt % to 15 wt % depending on the salinity and the temperature of the system, where the increase in salinity normally requires an increase in solids concentration for the stability of the emulsion to be increased.

[0015] According to yet another embodiment, the plurality of tracer agents are solid particles. These particles can be silica, synthesized copper, magnetite (Fe_3O_4), ferri/ferrous chlorides, barium iron oxide ($BaFe_{12}O_{19}$), zinc oxide, aluminium oxide, magnesium oxide, zirconium oxide, titanium oxide, cobalt (II) and nickel (II) oxide, barium sulfate ($BaSO_4$), etc. and the treatment fluid with the plurality of tracer agents is stabilized solution in aqueous fluids, solvent based fluids such as alcohols, [ethylene glycol], or hydrocarbon based fluids. The particles can be also of organic origin such as co-polymer suspensions such as latex, polysteren beads x-linked with di-vinyl benzene and others. Pyrolectric and piezoelectric crystals may also be used in the compositions herein.

[0016] The treatment fluid comprising a plurality of tracer agents is provided by mixing the treatment fluid with the plurality of tracer agents by means of a generator placed in the wellbore or by surface located equipment.

[0017] The treatment fluid comprising a plurality of tracer agents can be injected continuously during the treatment duration or periodically.

[0018] The treatment fluid comprising a plurality of tracer agents can be injected at any stage of the treatment including pre and post-treatment injection, during the complete treatment or partially.

[0019] The injection into the formation may be complemented with physical treatment such as vibration, heating acoustic treatments performed before, during or after the injection process is performed.

[0020] In another embodiment, the method can include adding to the treatment fluid comprising a plurality of tracer agents one or more additives selected from a group comprising gelling agents, foaming agents, friction reducers, surfactants, demulsifiers, inhibitors.

[0021] Physical properties of the formation are acoustic impedance and/or electric conductivity and/or magnetic permittivity, nuclear magnetic resonance (NMR) response, thermal propagation and hydrodynamic flow capabilities.

[0022] The detecting of physical properties of the formation is made by seismic, acoustic, electrical, electrokinetical, thermal, NMR, neutron or gamma-ray means that can be located on the surface and/or wellbore or cross wellbore.

[0023] The treatment fluid with the plurality of tracer agents can be flowed back from the subterranean formation and analyzed for changes in the tracer agents concentration, size, type and distribution function between the injected and produced treatment fluid.

[0024] The analysis of the changes in the tracer agents concentration, size and type distribution function between the injected and produced treatment fluids can be performed while flowing in the formation by the acoustics, electric, thermal, neutron or gamma-ray logging or by comparing samples of the injection and produced fluids.

[0025] Another aspects and advantages of the invention will be apparent from the following description and the appended claims.

DETAILED DESCRIPTION

[0026] A treatment fluid comprising a plurality of tracer agents, wherein each tracer agent is an object of submicron scale, is injected into the wellbore and the formation. Typical diameter/length dimension of a tracer agent is within the range between 1-1000 nm.

[0027] The injection or flow of objects of submicron scale (so called nano-tracers) that are contained within the treatment fluid serve as markers/tracers because their property of staying in bulk of the transport fluid without gravity segregation and no change in type of distribution function of the markers within time of the duration of the formation treatment and measurement operation. Further the nano-tracers have the main advantage that because of their size will occupy the whole volume that the fluid has created in the formation, including pore space or ultra small fissures where the fluid leaked off. This is in particular important in matrix acidizing where fluid is injected into pore space or in shale gas fracturing where swarms of fissures are created in the process of hydraulic fracturing. In contrary to the microseismic measurements in the shale fracturing where the registration of events is scarce and not necessary related to the treatment fluid propagation within the formation and hence the monitoring is therefore incomplete, the proposed method would allow for complete coverage of the hydraulically created fracture area.

[0028] Here the micro and nano-mixtures refer to a portion or full volume of the treatment fluid mixture of:

- **[0029]** Gas and liquid, whereas the gas is a low or no soluble gas bubbles in the liquid and liquid can be any mixture of water, brine, acids, hydrocarbons with any combination of additives such but not limited to as gelling agents, foaming agents, friction reducers etc. Gas used can be hydrocarbon gas such as methane or higher molecular weight hydrocarbon gas, nitrogen or other inorganic gas or mixtures of thereof. The liquid phase is the prime phase and the gas the secondary phase dispersed in the mixture with known size distribution, and life span and determines the physical and chemical properties of the mixture;
- **[0030]** Liquid-Liquid, so-called an emulsion which can be a presence of the high viscous liquid inside the low viscous liquid, as well as the presence of smaller droplets inside the larger one called double, triple etc. emulsion;
- **[0031]** Liquid-solids, where the presence of the solid object inside the main liquid phase can be produced by the introducing the solid particles, crystallization, chemical reaction, biological processes etc. The tracer agents can be of various shapes, ellipsoid, plate or needle-like, spherical, irregular etc. depending on the material used.

[0032] The creation of the treatment fluid with the plurality of tracer agents is carried out by either down-hole nano-tracers mixture generator placed in the wellbore or by surface located equipment which can be in form of generators or various types of tanks or canisters supplying the volume required for injection of the mixture. The example of such surface generator of nano bubbles is well explained in U.S. Pat. No. 7,059,591. Various fine size bubble generators are described in Japanese Patent Application Publication No. 2001-276589. 2002-11335, 2002-166151, and No. 2003-117368, Japanese Patent No. 3682286, EP application 2020260 and similar can be envisioned.

[0033] The generation of solid nano particles is explained in several instances and also in US patent application No. 2009/0107673 and PCT patent No. WO2009/079092.

[0034] The mixture can be injected continuously during the treatment duration or periodically at any rate and concentration. The mixture can be injected at any stage of the treatment including pre and post-treatment injection, during the complete treatment or partially. The injection into the formation may be complemented with physical treatment such as vibration, heating, acoustic treatments performed before, during or after the injection process is performed. The mixtures can be different in terms of type of base fluid and/or gas utilized for each treatment, or during the stage of the treatment allowing to distinguish the various stages within the single treatment or the multiple treatments within the same wellbore or the multi-wellbore completion.

[0035] Thereafter measurements are then performed to determine the location and distribution of the treatment fluid and to evaluate its geometric distribution and diversion by the means of measuring the change in physical properties of porous environment of the formation and placed hydraulic or natural fractures and fissures. It also allows monitoring and evaluating of near wellbore and wellbore processes and fluid placements such as fracturing, frac-pack treatments, matrix acidizing, scale inhibition squeezes, gravel packing, sand control and cementing and drilling fluids flow and placement of other various chemical and physical treatments of underground formation such as injection of surfactants, wetability modifiers, demulsifiers, alcohols, solvents, hot water or hot chemical injections, under positive pressure compared to the formation pressure.

[0036] The detection and measurement mechanism is based on seismic, acoustic, electrical, electrokinetical, thermal, neutron and gamma-ray measurements that can be conducted from surface and/or wellbore or cross wellbore.

[0037] In the instance where formation and treatment fluid is flown back to the wellbore and then to the surface the fluid and nano-tracers can be analyzed for changes in the tracers concentration, size, type (if multiples types of mixtures of different markers are used) distribution function between the injected and produced fluid. The analysis can be performed either downhole or at surface with the adequate method of the analysis depending on the nature of the markers used. The analysis can then provide additional information on the space that the tracers have occupied such but not limited to the permeability and conductivity of the fracture, effective permeability of the formation, the fluids that the markers interacted with and the PVT conditions they were exposed, the amount of fluid returned to surface vs. the amount of fracturing fluid that has leaked off.

[0038] The nano-tracers can have various subsurface applications.

[0039] Different types of nano-tracers can be added to the proppant or to the fracturing fluid at different times during the placement of proppant or treatment fluids (such as main fracturing fluids, spacers or pre-flush or flush in proppant fracturing or acids, spacers, pre-flushes or flushes in acid fracturing) during or after the fracturing process. The injection can be done during the main fracturing treatments as well as during the test-fracturing that is typically performed before the main fracturing treatment (so called injection, calibration step rate tests or mini-frac tests), cool-down stages preceding the main frac treatment or even after the main fracturing treatment as post-treatment injection into the pre-existing fracture. Thereafter various measurements are then performed to detect where the fluid has been injected. The detection and measurement mechanism is based on seismic, acoustic, electrical, electrokinetical, neutron, thermal and gamma-ray measurements that can be conducted from surface and/or wellbore or cross wellbore.

[0040] Different types of nano-tracers can be added to the gravel and gravel pack fluids. Various measurements can be performed after the gravel packing operations to detect where the fluid and the gravel pack materials have been injected/placed. The detection and measurement mechanism is based on seismic, acoustic, electrical, electrokinetical, neutron, thermal and gamma-ray measurements that can be conducted from surface and/or wellbore or cross wellbore.

[0041] The nano-tracers can be mixed with acids, solid acids pre-flushes and flushes such as brines, solutions of surfactants, chemical washes, scale and asphaltene inhibitor and their solutions, solvents and demuslfiers, gases, foams, diverter materials (solids, liquid and gaseous) or other compounds used in the treatment sequence to track/monitor completion related operations. The measurements on the placement of the fluids allow for fluid placement and fluid diversion detection in wellbores, multi zone stimulation and treatments, injection monitoring and flowback of the treatment and reservoir fluids.

[0042] The release of tagging nano-tracers into the flow can be used to obtain flow velocity or flow profile. In inclined and horizontal wellbores indication of fluid stratification, phase flow, fluid lagging, or fluid flow directions can be interpreted.

[0043] Nano-tracers injection and/or release can be used for identification/monitoring, of flood front allocation, of various techniques of Enhanced Oil Recovery techniques, where water, foams, gases (nitrogen, carbon dioxide, steam and others), surfactants, miscible and immiscible hydrocarbon, are injected in injector wells and with or without additional application of heat to increase the recovery factor of the reservoir. While these techniques are widely used in the industry, further improvements in oil recovery can be achieved by monitoring the flood front and controlling and optimizing the injection and production system of the field or field sector.

[0044] Nano-tracers can be used to track fracturing fluids in tight gas shale where swarms of fissures are created in the process of hydraulic fracturing. In contrary to the microseismic measurements in the shale fracturing where the registration of events is scarce and not necessary related to the treatment fluid propagation within the formation and hence the monitoring is therefore incomplete and incorrect, the proposed method where the fracturing fluids contain nano tracers would allow for complete coverage of the hydraulically created fracture area.

[0045] Different nano-tracer types can be used in combination to perform any of the operations disclosed herein.

[0046] While the invention has been described with respect to a preferred embodiments, those skilled in the art will devise other embodiments of this invention which do not depart from the scope of the invention as disclosed therein. Accordingly the scope of the invention should be limited only by the attached claims.

1. A method of tracking a treatment fluid in a subterranean formation penetrated by a wellbore comprising the steps of:
- providing a treatment fluid comprising a plurality of tracer agents, wherein each tracer agent is an object of submicron scale,
- injecting the treatment fluid with the plurality of tracer agents into the well and the formation, and
- determining the location and distribution of the treatment fluid by detecting changes in the physical properties of the formation caused by the arrival of the treatment fluid comprising a plurality of tracer agents.

2. The method of claim **1** wherein the treatment fluid is selected from the group consisting of fracturing fluids, drilling fluids, acidizing fluids, injection fluids, brines and completion fluids, fluids for EOR/IOR including reservoir flooding fluids.

3. The method of claim **1** wherein the plurality of tracer agents are low or insoluble gas bubbles having a diameter not more than 500 nm, the treatment fluid is water- or hydrocarbon-based solution and the treatment fluid with the plurality of tracer agents is a highly dispersed gas-liquid mixture.

4. The method of claim **3** wherein the gas is selected from the group consisting of methane, higher molecular weight hydrocarbon gas, nitrogen or other insoluble inorganic gas or mixtures of thereof.

5. The method of claim **3** wherein the water-based solution additionally comprises electrolytes of ferrous ions, manganese ions, calcium ions, or any other mineral ion such that the electrical conductivity in the solution is not less than 300 μ8 Λ Λ;m.

6. The method of claim **1** wherein the plurality of tracer agents are high viscous liquid droplets having a diameter not more than 1000 nm, the treatment fluid is water- or hydrocarbon-based solution and the treatment fluid with the plurality of tracer agents is an emulsion.

7. The method of claim **6** wherein the high viscous liquid is crude oil or toluene.

8. The method of claim **1** wherein the plurality of tracer agents are solid particles and the treatment fluid with the plurality of tracer agents is a stabilized solution in aqueous fluids, solvent based fluids such as alcohols or hydrocarbon based fluids.

9. The method of claim **8** wherein the solid particles are selected from the group consisting of silica, synthesized copper, magnetite (Fe304), ferri/ferrous chlorides, barium iron oxide (BaFe12019), zinc oxide, aluminium oxide, magnesium oxide, zirconium oxide, titanium oxide, cobalt (II) and nickel (II) oxide, barium sulfate (BaS04), pyrolectric and piezoelectric crystals etc.

10. The method of claim **1** wherein the treatment fluid comprising a plurality of tracer agents is provided by mixing the treatment fluid with the plurality of tracer agents by means of a generator placed in the wellbore.

11. The method of claim **1** wherein the treatment fluid comprising a plurality of tracer agents is provided by mixing the treatment fluid with the plurality of tracer agents by means of the surface located equipment.

12. The method of claim **1** wherein the treatment fluid comprising a plurality of tracer agents is injected continuously during the treatment duration.

13. The method of claim **1** wherein the treatment fluid comprising a plurality of tracer agents is injected periodically during the treatment duration.

14. The method of claim **1** wherein the treatment fluid comprising a plurality of tracer agents is injected at any stage of the treatment.

15. The method of claim **1** wherein the injection of the treatment fluid is accompanied by physical treatment performed before, during or after the injection process.

16. The method of claim **15** wherein the physical treatment is vibration, or heating, or acoustic treatments.

17. The method of claim **1** wherein the treatment fluid additionally comprises one or more additives selected from a group comprising gelling agents, foaming agents, friction reducers, surfactants.

18. The method of claim **1** wherein physical properties of the formation are acoustic impedance and/or electric conductivity and/or magnetic permittivity, nuclear magnetic resonance (NMR) response, thermal propagation and hydrodynamic flow capabilities

19. The method of claim **1** wherein detecting of physical properties of the formation is made by seismic, acoustic, electrical, electrokinetical, NMR, thermal, neutron or gamma-ray means.

20. The method of claim **19** wherein detecting of physical properties of the formation is made by seismic, acoustic, electrical, electrokinetical, NMR, thermal, neutron or gamma-ray means located on the surface.

21. The method of claim **19** wherein detecting of physical properties of the formation is made by seismic, acoustic, electrical, electrokinetical, NMR, thermal, neutron or gamma-ray means located in the wellbore.

22. The method of claim **1** wherein the treatment fluid with the plurality of tracer agents is flowed back from the subterranean formation and analyzed for changes in the tracer agents concentration, size, type and distribution function between the injected and produced treatment fluid.

23. The method of claim **22** wherein analyzing changes in the tracer agents concentration, size and type distribution function between the injected and produced treatment fluids is performed while flowing in the formation by the acoustics, electric, thermal, neutron or gamma-ray logging.

24. The method of claim **22** wherein analyzing changes in the tracer agents concentration, size and type distribution function between the injected and produced treatment fluids is performed by comparing samples of the injection and produced fluids.

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