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(57)	Abstract	

The invention provides for the use of at least one salt as a water tracer compound, wherein said salt comprises at least one organic or inorganic cation and at least one inorganic anionic metal complex. Typically the tracer is used in industrial water or in a subterranean reservoir, such as in monitoring fluid flow in a petroleum or geothermal reservoir. The anionic metal complex is detected to monitor fluid flow. The invention further provides a method for tracking the flow of at least one fluid, said method comprising applying at least one salt comprising at least one organic or inorganic cation and at least one inorganic anionic metal complex to at least one known position along the flow of said fluid and monitoring for the absence/presence and/or concentration of said inorganic anionic metal complex in samples of said at least one fluid. Other aspects of the invention include compositions comprising the described salts in a slurry with proppant particles and methods for monitoring the integrity of an isolation plug. Aggregates comprising consolidated crystals of the described salts are also provided.

Tracers

Field of the invention

The invention relates to the use of tracers for monitoring the flow of fluids, particularly in subterranean environments. More particularly, the invention relates to thermally-robust tracers and to sources of such tracers to monitor and/or detect fluid flows in petroleum reservoirs/wells, shale reservoirs, groundwater reservoirs, geothermal reservoirs or in industrial processes.

Background of the invention

Tracer technology is used extensively in oil and gas exploration and recovery, and both radioactive and non-radioactive tracers that can be measured at low concentrations are applied. Tracer technology may also apply to geothermal reservoirs for monitoring flow paths of injected water, leakage into ground water etc.

In petroleum reservoir tracer studies the tracers may be injected as pulses in well-to-well studies for measuring flow paths, water velocities and water-swept volumes. Radioactive tracers can be measured at very low levels, but for public non-acceptance reasons these tracers have in recent years been replaced by chemical tracers that can be analysed at low concentrations using sophisticated analytical instrumentation (such as GC-MS, HPLC-MS, ICP-MS). One issue faced by such alternative tracers is that they must be naturally present in very low abundance in order to allow positive identification of the tracer at very low concentrations.

Many different organic compounds have been applied as tracers for such studies, among others fluorinated benzoic acids, naphthalene sulfonates and amino-naphthalene sulfonates (Serres-Piole *et al.*, *Guidelines. Journal of Petroleum Science and Engineering* 98-99 (2012) 22-39). However, the environmental acceptability of organic tracers is not always high, particularly those comprising halogenated substituents. Furthermore, in high temperature reservoirs (typically > 150°C) many of the organic chemical tracers used both in petroleum and geothermal reservoirs will be less suitable due to limited thermal stability.

When the degradation rate of a chemical tracer at the actual reservoir temperature is known, the recovered amount of the tracer can be calculated (Adams *et al.*, *Geothermics, Vol. 20, pp 53-66, 1991*). Such an approach can only be applied when the temperature is known and the decay rate is relatively low. Ideally, only compounds that are not broken down, not adsorbed and not precipitated should be applied in tracer studies where the purpose is to passively trace the flow of a single fluid phase like water.

Tracer sources may be placed in oil or gas production wells to monitor in-flow from the surrounding formation. For in-flow monitoring studies the tracers may be encapsulated in a polymer which is placed along the external surface of the production tube at different locations before completion of the well as described in US 6,645,769. The tracers can be attached to or encapsulated in polymers or in different types of particles, and the release of the tracers can be made dependent on type of fluid passing (oil or water), on chemical properties of the fluid (for instance pH or salinity) or, for example, on temperature. The

tracers are released into the passing fluids and by analysing the concentration of tracers in the produced water, the in-flow rate of fluids from the different zones can be calculated if the correlation between release rate and flow rate can be estimated. One frequently applied method is to place polymer rods containing the tracer outside the production tube imbedded in the sand screen. The amount of tracer that can be mixed into the polymer is, however, limited (5-10 % by weight). If a larger amount is used, the release rate may be too high, resulting in a short lifetime of the tracer source. Independently of absolute rate, the amount of tracer released at the start in such release systems is usually proportionally high, and will decrease exponentially due to the increased diffusion resistance through the micro pores formed in the polymer matrix. The release rate of the tracers from such a system may be difficult to estimate since the rate will depend on physical parameters of the polymer and the fluids as well as conditions such as temperature and pressure.

Hydraulic fracturing is frequently used for stimulating gas or oil production from petroleum reservoirs, and is particularly applied in connection with gas production from shale formations. A viscous fluid is pumped at high pressure into defined sections of the well, usually followed by ceramic spherical particles (proppants) to prevent the fractures from collapsing when production is resumed. The placement of tracer release particles in fractures located at different zones and with different tracers at each location in order to make identification of flow paths possible is described in several patents/publications (e.g., SPE 36675, US 9,290,689, US 3,987,850, WO 2010/140032 and WO 2014/207000).

The disadvantages of polymer-encapsulated or polymer-adsorbed tracer particles are also seen in the area of hydraulic fracturing. One disadvantage is that the particles may be crushed during the process of pumping the fracturing fluid containing proppants into the fractures. This will lead to premature release of tracer and reduction of the tracer release period available for tracer monitoring. The release of tracer from a solid polymer particle will be high at the start and decrease exponentially if the release is based on dissolution of the tracer from the matrix and also if the tracer release is based on diffusion of volatile compounds through a polymer matrix.

In patent WO 2014/207000 the tracer particles consist of mineral crystals with inclusions of a tracer compound. The tracer is released by dissolution of the crystals over time, or in the case of inclusion of gas tracers, the tracers may also diffuse out from the crystals at high temperatures. These materials are highly effective and offer many properties which are superior to previously utilised tracer sources. The amount of tracer that can be encapsulated into the crystals as described in WO 2014/207000 is however limited.

In WO 2016/118263 to Baker Hughes, inorganic anionic metal complexes are mentioned as possible tracers among others, because they have low background in the formation. But the complexes cited are all part of "soluble to very soluble" salts, and not "sparingly soluble" ones.

In WO 99/50634 to Betzdearborn, concerned with boilers leak detection, soluble tracers are required, and in fact only soluble to very soluble inorganic anionic metal complexes are cited.

In US 4,966,711 to Hoots, concerned with process monitoring thanks to tracers, soluble tracers are required, and the few inorganic anionic metal complexes cited are all soluble to very soluble.

In view of the above, it would be of considerable advantage to provide tracers for monitoring fluid flow in many situations, including subterranean reservoirs, which are more environmentally acceptable and/or more thermally stable than currently used tracers. It would be an advantage if such tracers were readily detectable at low concentration and naturally present at very low levels in the systems of interest. It would be a further advantage to provide tracers with a predictable and controlled rate of release, preferably with a non-exponential decrease in release rate over time. It would be a further advantage if the tracers could be used in high pressure and/or high temperature situations such as fracturing and/or in geothermal reservoirs.

Summary of the invention

The present inventors have now established that certain salts comprising inorganic anionic metal complexes can address some or all of the above issues.

In a first aspect, the invention therefore provides the use of at least one salt as a water tracer compound in monitoring fluid flow in a subterranean reservoir, wherein said salt comprises at least one organic or inorganic cation and at least one inorganic anionic metal complex.

In a particular embodiment, the invention provides the use in monitoring fluid flow in a subterranean reservoir, such as a petroleum reservoir or geothermal reservoir. Preferably, the invention provides the use in at least one tracer method selected from:

- i) well-to-well tracer studies of petroleum reservoirs;
- ii) in-flow monitoring of petroleum wells;
- iii) tracer studies in fractures of shale reservoirs;
- iv) tracer studies of groundwater flow; and/or
- v) tracer studies of geothermal reservoirs.

In a further aspect, the invention provides a method for tracking the flow of at least one fluid (e.g. within a subterranean reservoir), said method comprising applying at least one salt comprising at least one organic or inorganic cation and at least one inorganic anionic metal complex to at least one known position along the flow of said fluid and monitoring for the absence/presence and/or concentration of said inorganic anionic metal complex in samples of said at least one fluid.

In a further aspect, the invention provides a method for monitoring the integrity of an isolation plug in a petroleum reservoir or geothermal reservoir, said method comprising applying at least one salt comprising at least one organic or inorganic cation and at least one inorganic anionic metal complex upstream of said isolation plug and monitoring for the presence of said inorganic anionic metal complex in produced fluid from said reservoir.

In a further aspect, the invention provides a composition comprising a slurry of at least one salt and proppant particles in water, wherein said salt comprises at least one organic or inorganic cation and at least one inorganic anionic metal complex.

In a further aspect, the invention provides a container containing a salt, wherein the container is closed and porous, and wherein the pores in the walls of the container are such that dissolved ions can diffuse in and out but solid particles cannot, wherein said salt comprises at least one organic or inorganic cation and at least one inorganic anionic metal complex.

In a further aspect, the invention provides a process for producing the salt by means of mixing solutions of two or more salt precursors, wherein said salt comprises at least one organic or inorganic cation and at least one inorganic anionic metal complex.

In a further aspect, the invention provides an aggregate comprising a plurality of consolidated salt crystals, wherein in at least one dimension said aggregate has a size of at least 5 cm, and wherein said salt comprises at least one organic or inorganic cation and at least one inorganic anionic metal complex.

For all aspects of the invention, the metal from the said inorganic anionic metal complex is from Group 4, 5, 6, 7, 9-or 16 (VIa) of the periodic table but the inorganic anionic metal complex is not $\text{Co}(\text{CN})_6^{3-}$

For all aspects of the invention. the salt is sparingly soluble, and has a solubility in water of 10^{-1} to 10^{-8} g/100mL H_2O , preferably of 10^{-2} to 10^{-5} g/100mL H_2O , at 20°C and atmospheric pressure.

In a further embodiment applicable to all aspects of the invention, the salt is in a semi-crystalline or crystalline form, preferably crystalline form.

The features of the aspects and/or embodiments indicated herein are usable individually and in combination in all aspects and embodiments of the invention where technically viable, unless otherwise indicated.

Detailed description of the invention

In the present invention, salts comprising at least one organic or inorganic cation and at least one inorganic anionic metal complex are used as water tracer compounds. Broadly, the invention can be used in many applications where a predictable release of tracer is required. The invention is based on the solubility and/or dissolution of the salts in water and the monitoring and/or detection of the inorganic anionic metal complex down to low concentrations using analytical techniques.

Solubility and background concentration

The salts of the present invention (which are applicable to all aspects of the invention) may be applied in solution or as solids. Where the tracers are applied as solids, they are preferably selected such that they are not released into the fluid instantaneously, but rather are released over a period of time, depending upon the flow and/or conditions of the reservoir. This may be achieved by any appropriate method including several known in the art, such as polymer encapsulation. In the context of the present invention, however, it is

preferable that the salts are themselves selected to be only sparingly soluble (e.g. as described herein).

In one preferable embodiment, 50% of the tracer may be released over a period of 1 hour to 10 years, more commonly 1 hour to 5 years, preferably over a period of 1 day to 24 months (such as 1 day to 3 weeks, 1 week to 3 or 6 months or 1 month to 24 months), following (and especially during) contact with fluids within the reservoir. Contact with fluids within the reservoir may occur immediately upon placement of the compositions in the reservoir environment. However, that contact may also occur later if the salt is contained, for example within a device that can open the composition to the fluid environment of the reservoir at a later date or time upon for example meeting the targeted conditions of pH, temperature, or salinity. Similarly, if a composition is within a device that can intermittently place the composition in contact with fluids in the reservoir environment, then this time will be taken to be the duration for which that contact was maintained.

In the case of salts used to monitor the integrity of valves, caps or similar blockages of flow, the duration of contact may be longer because the compositions may be placed in a position where fluid is present but not flowing. In one embodiment, the compositions therefore release 50% of their tracer in the above time periods of contact with *flowing* fluid within the reservoir. In some appropriate uses and methods, however, the contacting may be for longer periods, such as 1 month to 10 years, preferably 3 months to 5 years. Such methods may in one embodiment include methods for monitoring the integrity of caps, valves or similar items. Conversely, where the composition is used directly in continuous contact with the fluids of the reservoir then typical periods are preferably shorter, such as 1 day to 3 years, preferably 1 week to 24 months, or 1 week to 12 months.

Many anionic metal complexes can form sparingly soluble salts with cations of other metals and/or with organic cations. By selecting different combinations of cations and anions the solubility of the salts can be modified to suit a particular application. Generally, for any single application of tracer, a single anionic metal complex will be used and will thus identify that application point and/or time. A single cation or a mixture of cations may be used in order to provide the appropriate solubility and/or release profile.

It can also be envisaged that soluble salts are used for 'pulse'-like monitoring of fluid flow, such as by administering a "bolus" or pulse of tracer in solution to a fluid flow and monitoring the transport and/or distribution of that fluid by monitoring the presence, absence and/or concentration of the anionic metal complex in samples from the flow or possible flow of that fluid.

Preferably, the salts of the present invention are sparingly soluble salts. A sparingly soluble salt is here defined as a salt with a solubility in the range of 10^{-1} to 10^{-8} g/100mL H₂O at 20°C and atmospheric pressure. Preferably, the salt has a solubility in the range 10^{-1} to 10^{-5} g/100mL H₂O, such as 10^{-2} to 10^{-5} g/100mL H₂O. Typical solubilities for example compounds useful in all aspects of the invention are, for example, SrMoO₄ with a solubility of 0.011 g/100mL H₂O at 20°C and atmospheric pressure, and SrWO₄ with a solubility of 0.0004g/100mL H₂O at 20°C and atmospheric pressure. A range of 0.0001 to 0.025g/100mL is thus useful.

It is preferable if the background concentration of the tracer (particularly the anionic metal complex part of the tracer) in the fluid to be monitored is low. This improves signal-to-noise ratio and allows positive identification of the tracer at very low concentrations. Background concentration is defined as the concentration of tracer compound (or the anionic metal complex) in the fluid to be measured prior to the addition of tracer. A low background concentration is here defined as a concentration of less than 10 µg/L (e.g. 0.001 to 10 µg/L, 0.001 to 10 ppb) of the anionic metal complex, such as less than 5 µg/L (5 ppb). Preferably, the background concentration is less than 1 µg/L (1 ppb) of the anionic metal complex. For some compounds, the background level may be even lower than 0.1 µg/l (0.1 ppb).

A balance between background concentration and solubility must be struck to ensure good signal-to-noise ratio and appropriate release time for a feasible amount of tracer compound applied. For example, the use of a salt which has a high background concentration and a low solubility may give analytical data with poor signal-to-noise ratio unless an onerously large amount of tracer is used. A salt with high solubility and low concentration will give a favourable signal-to-noise ratio, but the high solubility will result in the tracer salt being depleted rapidly.

Salts

The inorganic tracers, of all aspects of the present invention, have potential for being more thermally stable than their organic tracer counterparts. It is preferable, however, to monitor the anions and not cations since cations may be adsorbed to clay minerals in the reservoir rock. The salts of the present invention comprise at least one cation and an anionic metal complex. It is correspondingly the anionic metal complex which is preferably measured and/or monitored. As used herein, references to a "salt", "tracer" or "tracer salt" refer to the described salts of at least one cation and an anionic metal complex (or simply to the anionic metal complex in solution where context allows) unless specified otherwise.

The term 'salt' as used herein also encompasses solvates and hydrates of salts. For example, the solubility of a salt may potentially be tuned and/or affected by choosing certain hydrates or solvates to meet the specific requirements of the present invention. All suitable hydrates and solvates form embodiments applicable to any compatible aspect of the invention.

The salts of all aspects of the present invention comprise at least one organic or inorganic cation (i.e. at least one organic cation, at least one inorganic cation, or at least one organic cation and at least one inorganic cation). In the case of two or more cations, each cation may be selected independently from any suitable cations, such as those indicated herein. The cation may be, but is not limited to, an alkaline earth metal cation, such as a cation of Mg, Ca, Sr, Ba (and mixtures thereof), particularly Sr. Other cations, whether organic or inorganic, may be used providing the resulting salts meet the requirements of the present invention in terms of solubility and stability. Alkali metal cations, such as cations of Li, Na and/or K may be suitable, as may organic cations such as ammonium, alkylammonium, pyridine and/or substituted pyridine cations. Cations of other metals such as Pb, Zn and/or Ag may also be used and all cations may be used individually or in combination in order to achieve the desired solubility profile.

The salts of all aspects of the present invention comprise an inorganic anionic metal complex. Preferably, the metal of said inorganic anionic complex is a metal from group 4, 5, 6, 7, 9 or 16 (Vla) of the periodic table. The metal is more preferably selected from the group consisting of Se, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Co, Rh and Ir. Even more preferably, the metal is a group VI or a group VII metal, such as Mo, W or Re. The use of crystal salts of two mutually soluble endmember anions (whilst sharing one common crystal structure), as in the SrMoO_4 - SrWO_4 series exhibiting different endmember solubilities, may also be applied for fine tuning of solubility behaviour, thus resulting in the release of two tracer anions, generally in known proportions.

In one embodiment applicable to all aspects of the invention, the inorganic anionic metal complex is a complex of a metal as hereinbefore defined with at least one X-type ligand.

In a further embodiment, applicable to all aspects of the invention, the inorganic anionic metal complex is a complex of a metal as hereinbefore defined with at least one anionic ligand selected from oxide, hydroxide, halide (e.g. fluoride, chloride, bromide or iodide), thiocyanate, and/or cyanide, preferably oxide. The complex may comprise one or more ligands of the same sort, or two or more different ligands (e.g. more than one halide or mixed oxide and cyanide ligands). It is a feature of the invention that the ligands in the anionic metal complex are not organic. However, carbon containing 'inorganic' ligands (e.g. cyanides, and/or thiocyanates) may be used. Some metal oxygen anions tend to be more stable than their corresponding cyanide, thiocyanate or halogen complexes.

In one preferable embodiment, the complex is not a metal cyanide (i.e. does not contain solely cyanide ligands and preferably does not contain any cyanide groups). More preferably the inorganic anionic metal complex is an anionic metal oxide or halide, preferably an anionic metal oxide. The risk that the anions can be precipitated with cations in produced water or react in other ways with chemical compounds present (H_2S in particular) must also be taken into account when selecting the particular combinations of metals and ligands.

In a preferred embodiment applicable to all aspects of the invention, the anionic inorganic metal salt is of the formula MO_3^{n-} or MO_4^{n-} (M = group VI or group VII metal, $n = 1$ or 2). Of these two formulae, MO_4^{n-} is in general preferred due its higher stability in water solutions compared to MO_3^{n-} . In particular, the complexes MoO_4^{2-} , WO_4^{2-} and ReO_4^- are particularly suitable for the present invention. Any other suitable inorganic anionic metal oxide may be used in any aspect of the invention providing it satisfies the requirements of the present invention in terms of, for example, solubility, stability, ease of detection and low background concentration. The choice of cation is important for the control of solubility. For instance, alkaline earth metals will form sparingly soluble salts with molybdate (MoO_4^{2-}) and tungstate (WO_4^{2-}), while perrhenate (ReO_4^-) may form sparingly soluble salts with organic cations such as tetraphenylpyridine.

The salts of the invention may be used as amorphous, semi-crystalline or crystalline solids. Preferably, the salts are used in semi-crystalline or crystalline form, more preferably crystalline form. By a semi-crystalline salt is meant a structure which comprises crystalline and amorphous regions. Even for completely crystalline solids, the degree of structural perfection may vary. Therefore, in the present invention, 'crystals' are here understood to encompass polycrystalline structures, 'twinned' structures and/or structures containing any

other crystallographic defects. The crystalline material can be crushed and sieved to desired grain sizes to ensure predictable release properties. Preferably, the salts used in the present invention may be used as crystalline particles having a size of no less than 10 μm (e.g. 10 μm to 200 μm), preferably no less than 100 μm (e.g. 200 μm or greater) and more preferably no less than 1mm in smallest dimension.

In any appropriate aspect of the present invention, such as when applied to in-flow tracer studies, the salts of the invention as described herein can be consolidated into aggregates, such as rods or bars, that can be placed in the reservoir, for example under the sand screens. Consolidation of crystals can be performed by filling a suitable mould with the crystals and slowly pumping through a saturated solution of the same salt that the crystals consist of. Precipitation from this saturated fluid will act as a bonding agent making the tracer crystals stick together. The resulting rod, bar or other solid shape will resemble the crystals in a lump of sugar, thus producing large bars or pieces of crystal, which may be formed in a shape appropriate for application and/or may be easily manipulated into place. Variations of temperature may be used to aid such a process, such as by applying hot saturated solutions and cooling these in a mould containing crystalline material to accelerate precipitation of further salt material. Evidently, this "binder" salt may be the same salt as the tracer, or may be another salt used to control strength and/or solubility of the final product or of the tracer material. The aggregate may have any size suitable for the intended use and its shape will be determined by the mould used. For example, the aggregate may be a block, rod, bar or any other shape. Preferably, in the smallest dimension the aggregate will have a size of at least 0.5mm, such as at least 1 mm. Preferably, in one of the dimensions, the aggregate will have a size of at least 5 cm, such as at least 10 cm, at least 50 cm or even at least 1m. Rods are a particular embodiment of this invention and may have a length of at least 1 cm, such as at least 10 cm, preferably at least 50 cm, more preferably at least 1m. For example, the rods may have the dimensions of around 2mm \times 7mm \times 1m.

The salts of the present invention are attractive for use in subterranean reservoir studies because of their thermal stability compared to other tracers, such as organic tracers. It is preferable if the salt is stable as a solid or in solution (e.g. in the fluid to be monitored) at a temperature of 100°C or more, preferably 150°C or more, more preferably 200°C or more, and even more preferably 250°C or more. By 'stable' is meant a degradation of less than 10% (e.g. 0.01% to 10%), preferably less than 5% over a period sufficient for use as a tracer. Such a period may be, for example at least 1 day (e.g. 1 day to 10 years). Preferably the salts will be stable (as described above) for at least 1 month, preferably at least 3 months, or at least 6 months, more preferably at least 1 year or at least 2 years. Where salts (especially sparingly soluble salts) are applied for long-term monitoring (e.g. of fluid flow) it will be preferable that those salts are stable for at least 2 years, preferably at least 5 years or at least 7 years. The required stability of the salt will depend on the intended use.

In one aspect, the present invention provides a composition comprising a slurry of at least one salt and proppant particles in water, wherein said salt comprises at least one cation and at least one inorganic anionic metal complex as hereinbefore defined. Said proppant particles may be selected from sand, resin-coated sand, bauxite, ceramics or mixtures thereof. The composition may further comprise at least one chemical agent commonly used

in fracturing fluids, such as a gel, foam, compressed gas, cleaning agent (e.g. acids), sodium chloride, a friction reducer (e.g. polyacrylamide), a scale deposit preventing agent, a viscosity modifiers/stabilizer, a compound for maintaining effectiveness of crosslinkers (e.g. carbonates), a disinfectant, a gelling agent, an anticorrosion agent and/or a winterizing agent.

In US5246861, potassium cobalt hexa-cyanide ($K_3[Co(CN)_6]$) is applied as a non-encapsulated tracer. However, the use of such a compound as a tracer has drawbacks. The tracer was found to have limited thermal stability under petroleum reservoir conditions (> about 100°C). The solubility properties of this salt may also limit its usefulness, particularly for methods utilising solid tracers (e.g. in crystalline form).

Containers

Crystals or amorphous particles of the sparingly soluble salts can be filled into microporous tubes or containers (the tubes or containers may suitably be formed from polymer, ceramic or sintered metal). The walls of the tubes or containers have pores communicating between the inside and the outside of the container such that dissolved ions can diffuse in and out while the solid particles remain inside. The pore size can be in the range 1-200 μm , preferably 5-100 μm , such as 10-50 μm or 30-70 μm in average largest diameter. The choice of porous wall material can be adapted depending on the size of the salt particles (whether crystalline, semi-crystalline or amorphous). The containers will typically be "closed" in the sense that no opening much greater than the pore size (e.g. no opening more than 10x, preferably no opening more than 2x the average pore size) is present.

The tubes or containers can be placed at specific locations in petroleum wells, for instance along the outer surface of the production tubing imbedded in the sand screens as described in US 6,645,769 B2 or in plug leak detection tools and deployment valves as described in WO 2014/207000 A1. Such containers with walls of microporous polymer, containing particles of sparingly soluble tracer crystals, may also be applied as tracer sources in a variety of other industrial processes, including those described herein.

Grains of sparingly soluble salts of the mineral tracer crystals can also be mixed into gravel packs and be used as tracer sources in a similar way as when placed in microporous tubes, bags or other type of containers.

Preparation of salts

The salts of the present invention may be prepared by any conventional means in the art. Preferably, the process for preparing the salt will be such that a semi-crystalline or crystalline, preferably crystalline, material is formed. In one embodiment the desired tracer salt is formed by means of mixing solutions of two or more salt precursors and forming the product by thermodynamically optimized reactions. The desired salt may be formed by a salt metathesis reaction (e.g. of the form $A-B + C-D \rightarrow A-D + C-B$). If the reaction is performed in a water solution, it is preferable that the process for forming the salt is such that the desired product precipitates, or preferably crystallizes, out of the water solution upon mixing of the reagents due to the low solubility of the product. Slow mixing of dilute solutions is preferred to ensure good crystal growth. By slowly mixing dilute solutions of, for instance, SrCl_2 and Na_2MoO_4 together, crystals of SrMoO_4 can be formed.

As well as the slow mixing of dilute water solutions of salt precursors, crystal growth can also be achieved after heating salts containing the desired elements with a fusing agent (Borax, LiCl etc.). For instance large crystals of SrWO_4 may be produced after heating solid SrCl_2 and solid $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ to above the melting point using LiCl as a flux agent followed by slow cooling from 950°C to 600°C over a period of 48 hours (see Figure 2).

The crystalline material can be crushed and sieved to desired grain sizes. If the tracers are placed along the production tube in the form of crystals that have a known solubility at the actual temperature, the release rate will be easier to estimate.

Detection/monitoring

The metal anionic complexes can be analysed/detected in water samples (from produced water, water from geothermal reservoirs, ground water extracted for drinking purposes etc.) using any suitable analytical method. Suitable analytical methods for the various embodiments of the invention include spectrometric methods and/or chromatographic methods, e.g. HPLC (high performance liquid chromatography) and/or MS (mass spectrometry), such as hyphenated high performance liquid chromatography and inductively coupled plasma mass spectrometry (HPLC-ICP-MS). If the metallic element is not present in other ionic forms in the water samples, ICP-MS may be used directly. However, any other form or combination of spectrometry, chromatography and/or other technique (e.g. spectroscopy) may be used.

In a preferred embodiment of the invention, the tracers are not radioactive tracers due to environmental and public non-acceptance reasons and are hence not detected by radioactive methods. However, such radioactive compounds and detection methods are not outside the technical scope of the invention. If appropriate, the inorganic anionic metal complexes may be detected by radiation detection, e.g. gamma-ray spectroscopy. It is also possible to apply metal anionic complexes where the said metal is enriched in one or more of the natural stable isotopes. The isotopic composition of the tracer metal element in the samples can be analysed using high resolution mass spectrometry, and the presence of the tracer can be verified and the concentration calculated. The application of special isotopes of the metal elements may result in a larger number of available tracers and allows for more than one tracer salt where each salt is identifiable but all have the same solubility characteristics, allowing for more direct comparison of fluid flow at multiple sites. Molybdenum for instance has 7 stable isotopes and tungsten has 5. In a corresponding embodiment, therefore, any of the salts indicated herein employed in any of the embodiments described may be enriched or depleted above or below natural abundance of at least one metal isotope. Such an enhancement or depletion may be by, for example, by at least 10% (e.g. 10 to 90%), at least 20%, at least 50% or at least 70% of the total isotopic content of that element in the salt.

Applications

The tracers of the invention are useful and utilised in various applications, particularly when applied to subterranean (which may also be taken as under the sea bed) reservoirs. Such reservoirs typically produce oil and/or gas, but may equally be geothermal reservoirs producing hot water and/or steam. The various aspects of the invention may be implemented in one or more of many ways. Thus, for example, in all aspects of the invention the tracers / compositions may be applied within completion equipment such as sand filter sleeve, may be placed into fractures or in the annulus and/or may be placed on the surface of tubulars. In one embodiment, the tracers may be put in place during the process of hydraulic fracturing, for example in the fracturing of shale deposits. This may be, for example, by including the tracers of the invention in the fracturing fluid and/or with the proppants (e.g. in the form of compositions containing tracers and proppants as described herein).

Well-to-well tracer studies of petroleum reservoirs

In one embodiment applicable to all aspects of the invention, water soluble salts of anionic metal complexes are used as tracers for well-to-well studies in petroleum reservoirs. Tests have shown that the background concentration of for instance the anions MoO_4^{2-} , WO_4^{2-} and ReO_4^- in produced water from petroleum wells is low (usually $<10\mu\text{g/l}$), and it is anticipated that the same will be the case for a number of other metal oxygen or halide anionic complexes.

Tracer studies of geothermal reservoirs

In *geothermal* reservoir management it is in many cases essential to re-inject the produced fluids in order to maintain the reservoir pressure and to have a means of disposing of fluids that may potentially be hazardous to the environment. The location of the injection well is crucial for a successful exploitation of the geothermal energy, and tracer technology can be utilised to reveal the flow patterns of the injected fluids for optimal and sustainable heat extraction. Solutions of water soluble salts of at least one organic or inorganic cation and at least one inorganic anionic metal complex as described herein (e.g. salts of metal oxygen anionic complexes) can be applied for such studies. These tracers may have a better thermal stability than the organic based tracers applied today, and may be applied in high temperature (typically $> 250^\circ\text{C}$) reservoirs where organic tracers may have limitations due to lack of thermal stability. In one embodiment, the salts of at least one organic or inorganic cation and at least one inorganic anionic metal complex are utilised in subterranean reservoirs at temperatures greater than 150°C , (e.g. greater than 200°C or greater than 250°C).

In-flow monitoring of petroleum wells

When the tracer is applied in the form of a crystal, where the crystal itself is formed largely or exclusively of the tracer compound, the amount of tracer available will be high compared to the situation where the tracer is mixed into a polymer or other type of matrix. The release rate will depend on the solubility of the salt applied at the actual temperature and will also to some extent depend on concentration of other salts and of the flow rate of the passing fluids. If the tracers are placed along the production tube in the form of mineral crystals (e.g. of the salts described herein) that have a known solubility at the actual temperature (i.e. the temperature of the fluid at the point of monitoring, such as within the subterranean reservoir), the release rate will be easier to estimate. The release rate will not decrease exponentially with time, but will only decline slowly as the surface area of the particles gradually becomes smaller. Since in one embodiment the salts are sparingly soluble (e.g. as described herein), the solubility of the salt is limited and the dissolution of the crystals will largely depend on the flow rate of the passing fluids. Stationary fluids becoming saturated with tracer salt before a large proportion of that salt has been dissolved.

Crystals or amorphous particles of the sparingly soluble salts can be filled into microporous polymer tubes or containers. The tubes or containers may also be ceramic or metal-sintered containers. The walls of the tubes or containers have pores where dissolved ions can diffuse in and out while the solid particles remain inside and such tubes or containers will typically

have pore sizes as described herein. The tubes or containers can be placed at specific locations in petroleum wells, for instance along the outer surface of the production tubing imbedded in the sand screens as described in US 6,645,769 B2 or in plug leak detection tools and deployment valves as described in WO 2014/207000 A1. Grains of sparingly soluble salt tracers can also be mixed into gravel packs and be used as tracer sources in a similar way as when placed in microporous tubes, bags or other type of containers. Such containers with walls of microporous polymer containing particles of sparingly soluble tracer crystals may also be applied as tracer sources in a variety of other subterranean and industrial processes. The tracer salt will slowly be dissolved into the passing water flowing from the formation into the well.

In the case of two or more gravel packs containers, these are located at different zones during the completion of the well and may contain different types of sparingly soluble tracer salts (particularly salts formed of different anionic metal complexes). When the particles are slowly dissolved in the passing fluids and the tracer anions are transported out and analysed in the produced water, valuable information concerning water production from different zones can be obtained. Analysis of the concentration of the anionic metal tracer complexes in the produced water will make calculation of in-flow from different zones possible.

Application of tracer crystals in fractures of shale reservoirs

Hydraulic fracturing is used for stimulating gas or oil production from petroleum reservoirs especially in shale formations. A viscous fluid is pumped at high pressure into defined sections of the well, usually followed by particles of robust materials such as ceramic spherical particles (proppants) to prevent the fractures from collapsing when production is resumed. The placement of tracer release particles in fractures located at different zones and with different tracers at each location in order to make identification of flow paths possible is described in several patents (e.g. SPE 36675, US 9,290,689, US 3,987,850, WO 2010/140032 and WO 2014/207000). In patent WO 2014/207000 A1 the tracer particles consist of mineral crystal with inclusions of a tracer compound. The tracer is released by dissolution of the crystals over time, or in the case of inclusion of gas tracers, the tracers may also diffuse out from the crystals at high temperatures. The amount of tracer that can be encapsulated into the crystals as described in WO 2014/207000 A1 is however limited. When the tracer salt is in the form of crystals consisting of or consisting essentially of the tracer salt itself, the amount of tracer available in the fractures will be much higher. For injection into fractures in shale reservoirs with proppants a grain/crystal size similar to the particle size of the proppants will provide good results. If the size of the crystals of tracer is too large then these may be excluded from the fractures by their size. If, however, the sizes of the particles of tracer are too small then there is the possibility that the grains will be washed out from the fractures with the produced water. A size of 0.2 to 5 times the size of the proppant particles may be appropriate, preferably 0.5 to 2 times that size. When crystals containing different metal anionic complexes are injected into different zones of the well, important information concerning the amount of water production from the zones can be obtained. Injection of such sparingly soluble tracer crystals can also be used to detect leakage of fracturing fluids into surrounding water reservoirs (e.g. into ground water for other uses, such as drinking water).

Further applications

Other applications of the salts of the present invention will be evident to the skilled worker and include, for example, a method for monitoring and/or validating the integrity of an isolation plug in a petroleum reservoir or geothermal reservoir, said method comprising applying at least one salt as defined in the description or the claims herein on the downhole side (e.g. upstream) of said isolation plug and monitoring for the tracer complex in the produced fluid from said reservoir. Thus, this and each application of the salts form a further embodiment of the invention.

Other applications of the salts comprising a cation and anionic metal complex as tracers also form aspects of the present invention. For example, other applications include monitoring and/or validating reservoir layers separation in a multi-layer reservoir, for example after an operation of stimulation or injection of chemicals to provide a flow barrier, such as in US 2011,0277996. Monitoring geometry of a fracture, such as described in WO 2010/011402 is another. Monitoring and tracking backflow of proppants, such as described in WO 2005/103446 is another. Assessing recovery of material injected in a subterranean formation such as in WO 2002/095159 is another. Assessing the volume of fluid injection in a reservoir stimulation is yet another, such as described in WO 2011/141875.

Other uses for the soluble salts of the water tracers can be hydrological studies or various industrial processes where tracer technology can be applied. Suitable industrial processes include all processes where water is used, and in particular where water is stored, recovered or recycled such that the tracers of the present invention may be used to monitor flow or particularly leakage of water from the process. Processes such as power generation (solar, geothermal, fossil-fuel or nuclear powered) where heat transfer fluids are used are typical examples. Other relevant industrial processes such as those using water to cool cutting or milling operations (e.g. in metal working operations), where water acts as a carrier (e.g. paper making) or as a general coolant (e.g. in chemical industries or in moulding, casting or glassmaking operations) are also suitable for applying the various aspects of the present invention. Any of these fluids and those used in similar applications may be monitored in the various aspects of the present invention. In particular, the tracers may be used to detect leakage of industrial water and/or to monitor or detect contamination of land and/or ground-water with industrial water. Monitoring the fate of water discharged to the environment and/or of run-off water from farms, industrial land or through drains forms a further embodiment.

Brief description of drawings

Figure 1: Microscope photograph of SrMoO₄ crystals formed at 80°C by mixing solutions of 0.05M SrCl₂ and 0.05M Na₂MoO₄ over a period of 48 hours.

Figure 2: Microscope photograph of SrWO₄ crystals formed by precipitation after fusion with LiCl to 950°C and controlled cooling to 600°C over a period of 48 hours

Figure 3: Diagram showing concentrations of MoO_4^{2-} and WO_4^{2-} in the collected fractions after leaching with 4%NaCl solution from microporous polyethylene containers filled with SrMoO_4 and SrWO_4 crystals.

Figure 4: Overlaid chromatogram from HPLC-ICP-MS of ReO_4^- in a reference standard and 8 produced water samples from different petroleum fields.

Figure 5: Overlaid chromatogram from HPLC-ICP-MS of MoO_4^{2-} in a reference standard and 6 produced water samples from different petroleum fields.

Figure 6: Overlaid chromatogram from HPLC-ICP-MS of WO_4^{2-} in a reference standard and 6 produced water samples from different petroleum fields.

Examples of preparation

Example 1

Two polyethylene filter cylinders of length 46mm, outer diameter 6.45mm and internal diameter 3.20mm were filled with crystals of SrMoO_4 and SrWO_4 respectively. The cylinders had a pore size of 30-70 μm . The cylinders were filled with 4% NaCl-solution before the open end of the tubing was plugged with a silicon rubber stopper. The cylinders were placed in a glass column and the void volume of the column was filled up with 3mm glass beads. The column was placed in a heating cabinet adjusted to a temperature of 80°C, and artificial formation water containing 4% NaCl was pumped through the column at a flow rate of 0.1 mL/min. Fractions of the eluted NaCl-solution were collected on a daily basis for a period of 14 days, and the collected fractions were analysed by ICP-MS for the content of Mo and W. After about 5 days the concentration in the eluted fractions stabilized at about half of the initial value (Figure 3). After 14 days 0.98% of the total amount of SrMoO_4 had been dissolved, while the corresponding value for SrWO_4 was 0.91%. Calculated from the mean dissolution rate during this experiment, the live-time of the crystals can be estimated to about 200 weeks. It is anticipated that similar tracer crystals where Ba substitutes Sr (as BaMoO_4) will exhibit even longer lifetimes.

Example 2

Some produced water samples from different petroleum reservoirs around the world were analysed using HPLC-ICP-MS for the concentration of the metal oxygen anions MoO_4^{2-} , WO_4^{2-} and ReO_4^- . The content of ReO_4^- was found to be less than 0.1ppb for all samples tested. Overlaid chromatograms from HPLC-ICP-MS analysis of ReO_4^- in the 8 produced water samples and a standard solution are shown in Figure 4. MoO_4^{2-} was detected in one sample at 9 ppb, while in the other 5 samples tested the concentration was below 1ppb (See Figure 5). For WO_4^{2-} the concentration was found to be 13, 6 and 2 ppb respectively for three of the samples and <1 ppb for the three other samples (See Figure 6).

Claims

1. The use, , as a water tracer compound in monitoring fluid flow in a subterranean reservoir, of at least one salt comprising at least one organic or inorganic cation and at least one inorganic anionic metal complex, characterised in that the metal of said inorganic anionic metal complex is a metal from group 4, 5, 6, 7, 9-or 16 (VIa) of the periodic table but not $\text{Co}(\text{CN})_6^{3-}$, wherein the salt is sparingly soluble, and has a solubility in water of 10^{-1} to 10^{-8} g/100mL H_2O , preferably of 10^{-2} to 10^{-5} g/100mL H_2O , at 20°C and atmospheric pressure.
2. The use of Claim 1, wherein the metal of said inorganic anionic metal complex is a metal selected from Se, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Co, Rh and Ir.
3. The use of any preceding claim wherein the metal of said inorganic anionic metal complex is a group VI or group VII metal, preferably Mo, W or Re.
4. The use of any preceding claim in at least one tracer method selected from
 - i) well-to-well tracer studies of petroleum reservoirs;
 - ii) in-flow monitoring of petroleum wells;
 - iii) tracer studies in fractures of shale reservoirs;
 - iv) tracer studies of groundwater flow; and/or
 - v) tracer studies of geothermal reservoirs.
5. The use of any preceding claim wherein the salt is in a semi-crystalline or crystalline form, preferably crystalline form.
6. The use of any preceding claim wherein the anionic metal complex is a complex of a metal with at least one X-type ligand, and/or a ligand selected from oxide, halide (e.g. fluoride, chloride, bromide or iodide), thiocyanate, and/or cyanide, preferably oxide.
7. The use of Claim 6, wherein the anionic metal complex is a complex of a metal with at least one X-type ligand, and/or a ligand selected from oxide and halide.
8. The use of any preceding claim wherein the inorganic anionic metal complex is MoO_4^{2-} , WO_4^{2-} or ReO_4^- .
9. The use of any preceding claim wherein said cation is at least one inorganic and/or organic cation, preferably comprising at least one alkaline earth cation such as Mg, Ca, Sr, Ba, particularly Sr.
10. The use of any preceding claim wherein said inorganic anionic metal complex is stable as a solid or in solution at a temperature of at least 100°C, preferably at least 150°C, more preferably at least 200°C, and even more preferably at least 250°C.
11. The use of any preceding claim wherein the background concentration of inorganic anionic metal complex in the fluid to be monitored is of less than 10µg/L.
12. The use of any preceding claim wherein at least two different salts are applied to a reservoir wherein the at least two salts comprise different inorganic anionic metal complexes.
13. The use of claim 12 wherein each of the two or more salts are placed at a different location.

14. A method for tracking the flow of at least one fluid, characterised in that said method comprises applying at least one salt comprising at least one organic or inorganic cation and at least one inorganic anionic metal complex, to at least one known position along the flow of said fluid and monitoring for the absence/presence and/or concentration of said inorganic anionic metal complex in samples of said at least one fluid, and

wherein the metal of said inorganic anionic metal complex is a metal from group 4, 5, 6, 7, 9-or 16 (VIa) of the periodic table but not $\text{Co}(\text{CN})_6^{3-}$, wherein the salt is sparingly soluble, and has a solubility in water of 10^{-1} to 10^{-8} g/100mL H_2O , preferably of 10^{-2} to 10^{-5} g/100mL H_2O , at 20°C and atmospheric pressure.

15. A method for monitoring the integrity of an isolation plug in a petroleum reservoir or geothermal reservoir, said method comprising applying at least one salt comprising at least one organic or inorganic cation and at least one inorganic anionic metal complex upstream of said isolation plug and monitoring for the presence of said inorganic anionic metal complex in produced fluid from said reservoir,

wherein the metal of said inorganic anionic metal complex is a metal from group 4, 5, 6, 7, 9-or 16 (VIa) of the periodic table but not $\text{Co}(\text{CN})_6^{3-}$, wherein the salt is sparingly soluble, and has a solubility in water of 10^{-1} to 10^{-8} g/100mL H_2O , preferably of 10^{-2} to 10^{-5} g/100mL H_2O , at 20°C and atmospheric pressure.

16. The method of claim 15 wherein the presence of the tracer in the produced fluids is taken to indicate a leakage from said plug.

17. A composition comprising a slurry of proppant particles in water, characterised in that said composition further comprises at least one salt, wherein said salt comprises at least one organic or inorganic cation and at least one inorganic anionic metal complex, wherein the metal of said inorganic anionic metal complex is a metal from group 4, 5, 6, 7, 9-or 16 (VIa) of the periodic table but not $\text{Co}(\text{CN})_6^{3-}$, wherein the salt is sparingly soluble, and has a solubility in water of 10^{-1} to 10^{-8} g/100mL H_2O , preferably of 10^{-2} to 10^{-5} g/100mL H_2O , at 20°C and atmospheric pressure.

18. The composition of claim 17 wherein said proppant particles are selected from sand, resin-coated sand, bauxite, ceramics or mixtures thereof.

19. The composition of claim 17 or 18 further comprising at least one chemical commonly used in fracturing fluids, such as a gel, foam, compressed gas, cleaning agent, sodium chloride, a friction reducer, a scale inhibitor, a viscosity modifiers/stabilizer, a compound for maintaining effectiveness of crosslinkers, a disinfectant, a gelling agent, and anticorrosion agent and/or a winterizing agent.

20. A container containing a salt, wherein the container is closed and porous, and wherein the pores in the walls of the container are such that dissolved anionic inorganic metal complex can diffuse in and out but solid particles cannot, characterised in that said salt comprises at least one organic or inorganic cation and at least one inorganic anionic metal complex wherein the metal of said inorganic anionic metal complex is a metal from group 4, 5, 6, 7, 9-or 16 (VIa) of the periodic table but not $\text{Co}(\text{CN})_6^{3-}$, wherein the salt is sparingly soluble, and has a solubility in water of 10^{-1} to 10^{-8} g/100mL H_2O , preferably of 10^{-2} to 10^{-5} g/100mL H_2O , at 20°C and atmospheric pressure.

Patentkrav

1. Anvendelse som sporingstoff for vann for monitorering av fluidstrømmer i et underjordisk reservoar, av minst et salt som omfatter minst et organisk eller et uorganisk kation og minst et uorganisk anionisk metall-kompleks, karakterisert ved at metallet i nevnte uorganiske anionisk metall-kompleks er et metall fra gruppe 4, 5, 6, 7, 9 eller 16 (VIa) i det periodiske system, men ikke $\text{Co}(\text{CN})_6^{3-}$, hvori saltet er tungt løselig og har en løselighet i vann på 10^{-1} til 10^{-8} g/100ml H_2O , fortrinnsvis på 10^{-2} til 10^{-5} g/100ml H_2O , ved 20°C og atmosfærisk trykk,.
2. Anvendelse ifølge krav 1 i hvori metall-elementet i nevnte uorganiske anioniske metall-kompleks er et metall valgt fra Se, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Co, Rh and Ir.
3. Anvendelse ifølge hvilket som helst foregående krav hvori metall-elementet i nevnte uorganiske anioniske metall-kompleks er et metall fra gruppe VI eller gruppe VII, fortrinnsvis Mo, W eller Re.
4. Anvendelsen ifølge hvilket som helst foregående krav av minst en sporingstoff-fremgangsmåte valgt fra
 - i) Brønn-til-brønn sporingstoffundersøkelser av petroleumsreservoarer
 - ii) Måling av innstrømming av fluider i petroleumsbrønner
 - iii) Sporingstoffundersøkelser av oppsprekninger i skiferreservoarer
 - iv) Sporingstoffundersøkelser av grunnvannstrømmer; og/eller
 - v) Sporingstoffundersøkelser av geotermiske reservoarer.
5. Anvendelse ifølge hvilket som helst foregående krav hvori saltet er i en halvkrystallinsk eller krystallinsk form, fortrinnsvis krystallinsk form.
6. Anvendelse ifølge hvilket som helst foregående krav hvori det anioniske metall-komplekset er et kompleks av et metall med minst en X-type ligand og/eller en ligand valgt fra oksid, halogenid (det vil si fluorid, klorid, bromid eller jodid), thiocyanat, og/eller cyanid, fortrinnsvis oksid.
7. Anvendelse ifølge krav 5 hvori metall-komplekset er et kompleks av et metall med minst en X-type ligand, og/eller en ligand valgt fra oksid og halogenid.
8. Anvendelse ifølge hvilket som helst foregående krav hvori det uorganiske anioniske metall-komplekset er MoO_4^{2-} , WO_4^{2-} eller ReO_4^- .

9. Anvendelse ifølge hvilket som helst foregående krav hvori nevnte kation er minst et uorganisk eller organisk kation, fortrinnsvis omfattende minst et jordalkaliemettall slik som Mg, Ca, Sr, Ba, særlig Sr.
10. Anvendelse ifølge hvilket som helst foregående krav hvori nevnte uorganiske anioniske metall-kompleks er stabilt i form av fast stoff eller i løsning ved en temperatur på minst 100°C, fortrinnsvis minst 150°C, mer foretrukket minst 200°C, og ennå mer foretrukket minst 250°C.
11. Anvendelse ifølge hvilket som helst foregående krav hvori bakgrunns-konsentrasjonen av det uorganiske anioniske metall-komplekset i fluiden som skal måles er lavere enn 10 µg/l.
12. Anvendelse ifølge hvilket som helst foregående krav hvori minst to forskjellige salter anvendes i et reservoar hvor de minst to saltene omfatter ulike uorganiske anioniske metall-komplekser.
13. Anvendelse ifølge krav 12 hvori hver av de minst to saltene er plassert ved forskjellige lokasjoner.
14. En fremgangsmåte for sporing av strøm av minst et fluid, karakterisert ved at nevnte fremgangsmåte omfatter anvendelse av minst et salt som omfatter minst et organisk eller uorganisk kation og minst et uorganisk anionisk metall-kompleks, til minst en kjent posisjon langs strømmen av nevnte fluid og monitorering for fravær/tilstedeværelse og/eller konsentrasjon av nevnte uorganiske anioniske metall-kompleks i prøver av nevnte minst et fluid, og hvor metall-elementet i nevnte uorganiske anionisk metall-kompleks er et metall fra gruppe 4, 5, 6, 7, 9 eller 16 (VIa) i det periodiske system, men ikke $\text{Co}(\text{CN})_6^{3-}$, hvor saltet er tungt løselig og har en løselighet i vann på 10^{-1} til 10^{-8} g/100ml H_2O , fortrinnsvis på 10^{-2} til 10^{-5} g/100ml H_2O , ved 20°C og atmosfærisk trykk.
15. En fremgangsmåte for monitorering av funksjonaliteten av en tettingsplugg i et petroleumsreservoar eller geotermisk reservoar, nevnte fremgangsmåte omfatter anvendelse av minst et salt som omfatter minst et organisk eller uorganisk kation

og minst et uorganisk anionisk metall-kompleks opp-strøms fra nevnte tettingsplugg og monitorering for tilstedeværelse av nevnte uorganiske anioniske metall-kompleks i produsert fluid fra nevnte reservoar, hvor metall-elementet i nevnte uorganiske anioniske metall-kompleks er et metall fra gruppe 4, 5, 6, 7, 9 eller 16 (VIa) i det periodiske system, men ikke $\text{Co}(\text{CN})_6^{3-}$, hvor saltet er tungt løselig og har en løselighet i vann på 10^{-1} til 10^{-8} g/100ml H_2O , fortrinnsvis på 10^{-2} til 10^{-5} g/100ml H_2O , ved 20°C og atmosfærisk trykk.

16. Fremgangsmåten ifølge krav 15 hvori tilstedeværelsen av sporingstoffet i de produserte fluidene benyttes som indikasjon på lekkasje fra nevnte plugg.
17. En sammensetning som omfatter en oppslemming av proppant partikler i vann karakterisert ved at nevnte sammensetning videre omfatter minst et salt hvor nevnte salt omfatter minst et organisk eller uorganisk kation og minst et uorganisk anionisk metall-kompleks, hvor metall-elementet i nevnte uorganiske metall-kompleks er et metall fra gruppe 4, 5, 6, 7, 9 eller 16 (VIa) i det periodiske system, men ikke $\text{Co}(\text{CN})_6^{3-}$, hvor saltet er tungt løselig og har en løselighet i vann på 10^{-1} til 10^{-8} g/100ml H_2O , fortrinnsvis på 10^{-2} til 10^{-5} g/100ml H_2O , ved 20°C og atmosfærisk trykk.
18. Sammensetningen ifølge krav 17 hvori nevnte proppant partikler er valgt ut fra sand, resin-belagt sand, bauxitt, keramiske partikler eller en blanding av disse.
19. En sammensetning ifølge krav 17 eller 18 videre omfattende minst et kjemikalium vanligvis benyttet i fraktureringsvæsker slik som gel, skum, komprimert gass, rensesvæske, natriumklorid, et friksjonsreducerende middel, en avleiringshemmer, et viskositetsregulerende eller stabiliserende middel, et stoff for å bevare virkningen av kryssbindinger, et desinfeksjonsmiddel, en gel-danner og anti-korrosjon og/eller frosthindrende midler.
20. En beholder som inneholder et salt hvor beholderen er lukket og porøs og hvor porene i veggene i beholderen er av en slik beskaffenhet at oppløste anioniske uorganiske metall-komplekser kan diffundere inn og ut mens faste partikler ikke kan det, karakterisert ved at nevnte salt omfatter minst et organisk eller

uorganisk kation og minst et uorganisk anionisk metall-kompleks, hvor metall-elementet i nevnte uorganiske metall-kompleks er et metall fra gruppe 4, 5, 6, 7, 9 eller 16 (VIa) i det periodiske system, men ikke $\text{Co}(\text{CN})_6^{3-}$, hvor saltet er tungt løselig og har en løselighet i vann på 10^{-1} til 10^{-8} g/100ml H_2O , fortrinnsvis på 10^{-2} til 10^{-5} g/100ml H_2O , ved 20°C og atmosfærisk trykk.

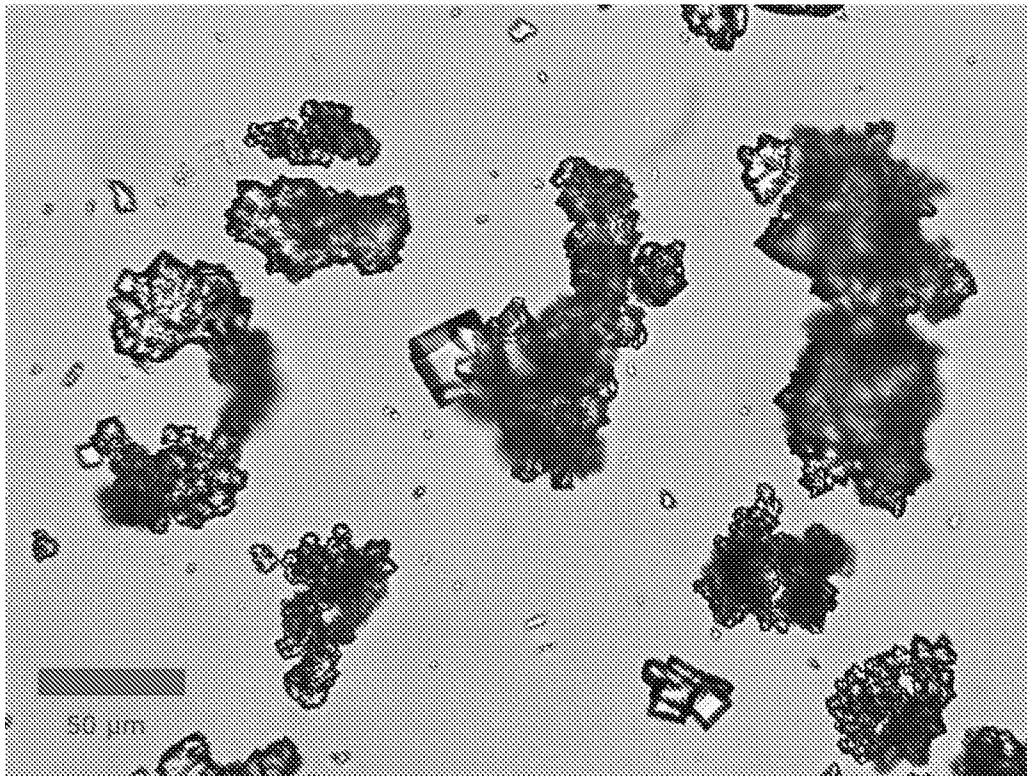


Figure 1

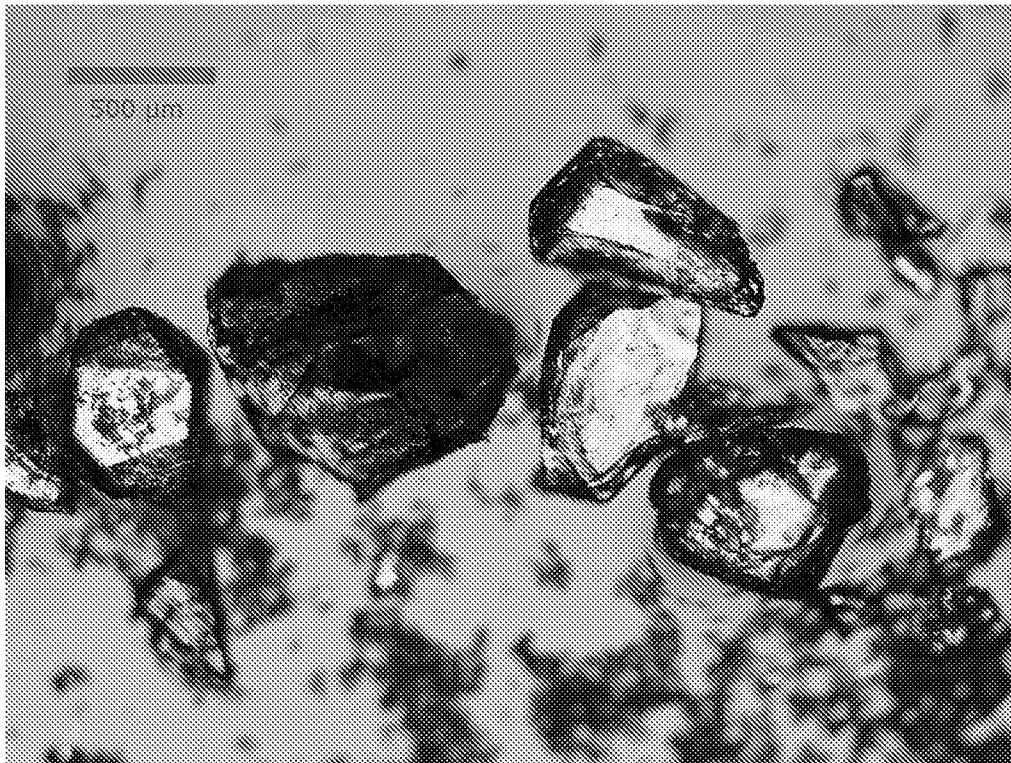


Figure 2

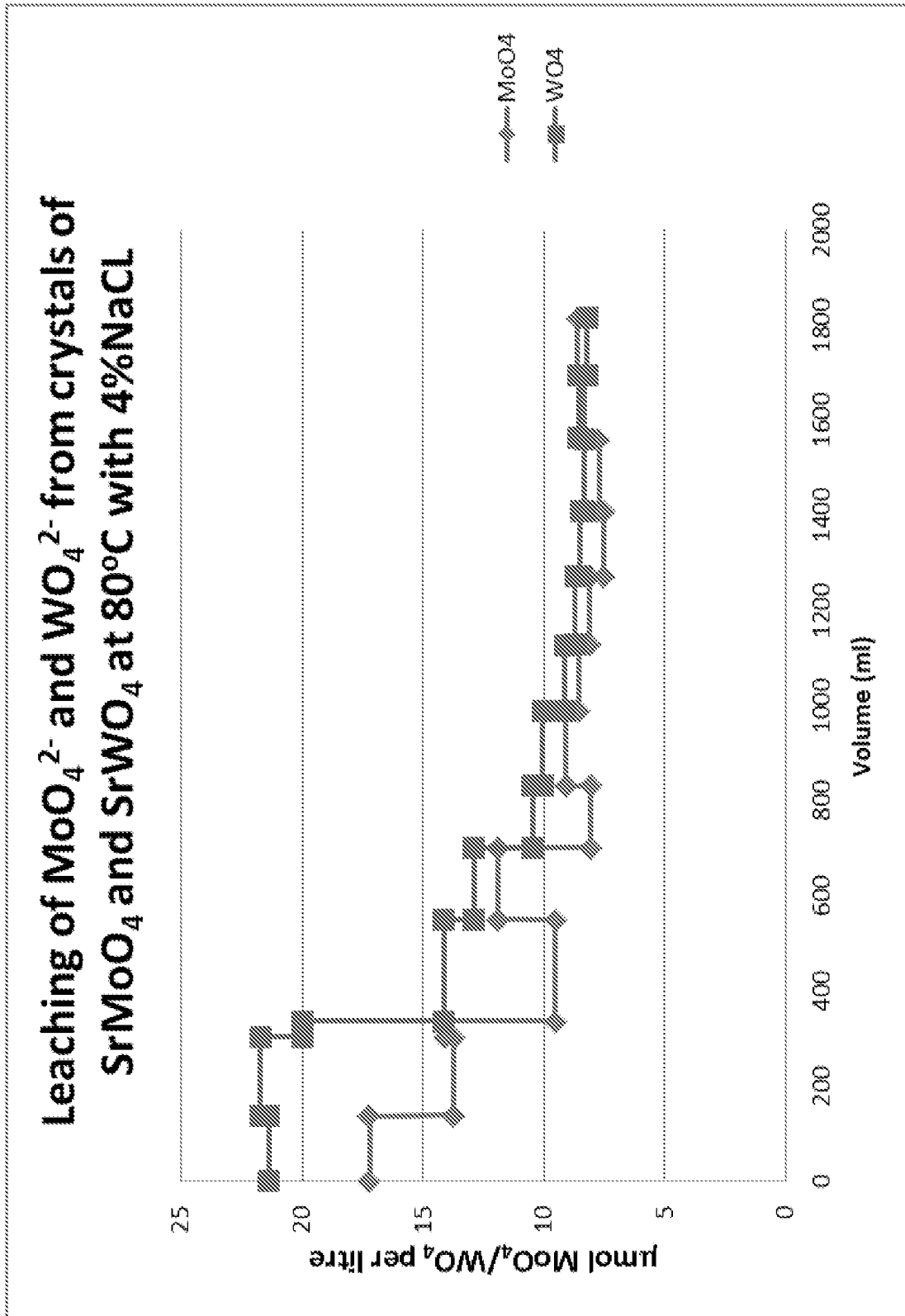


Figure 3

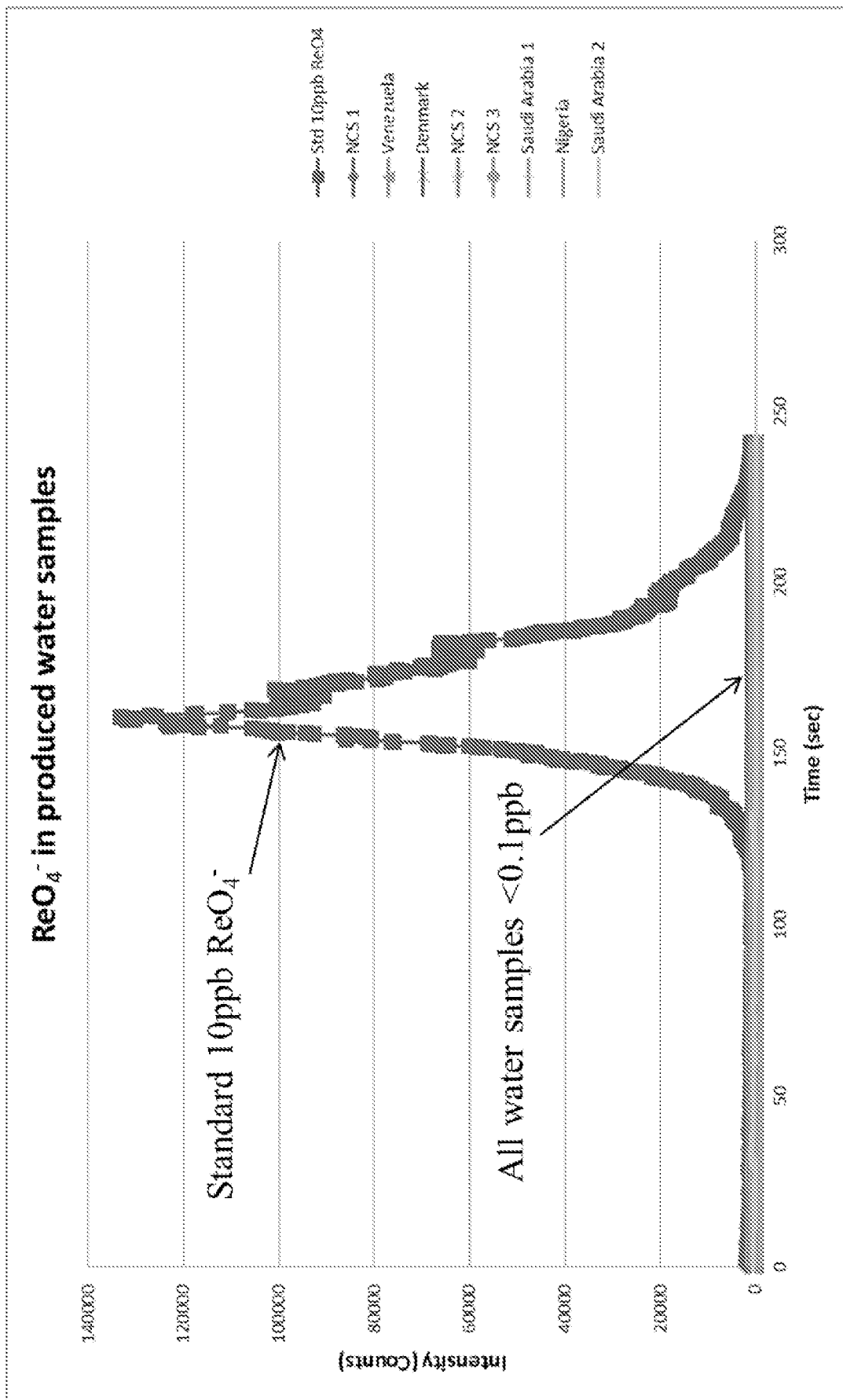


Figure 4

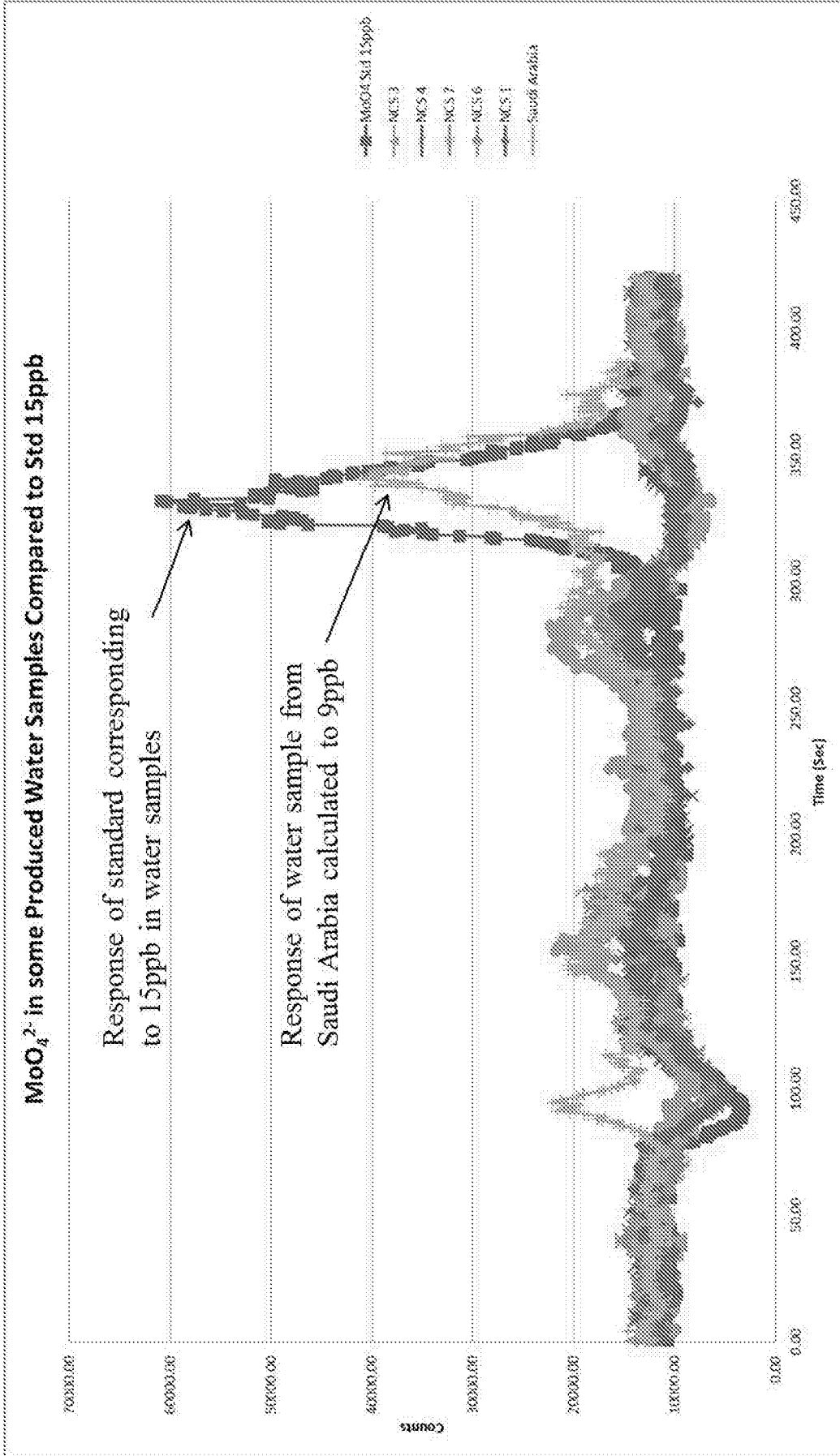


Figure 5

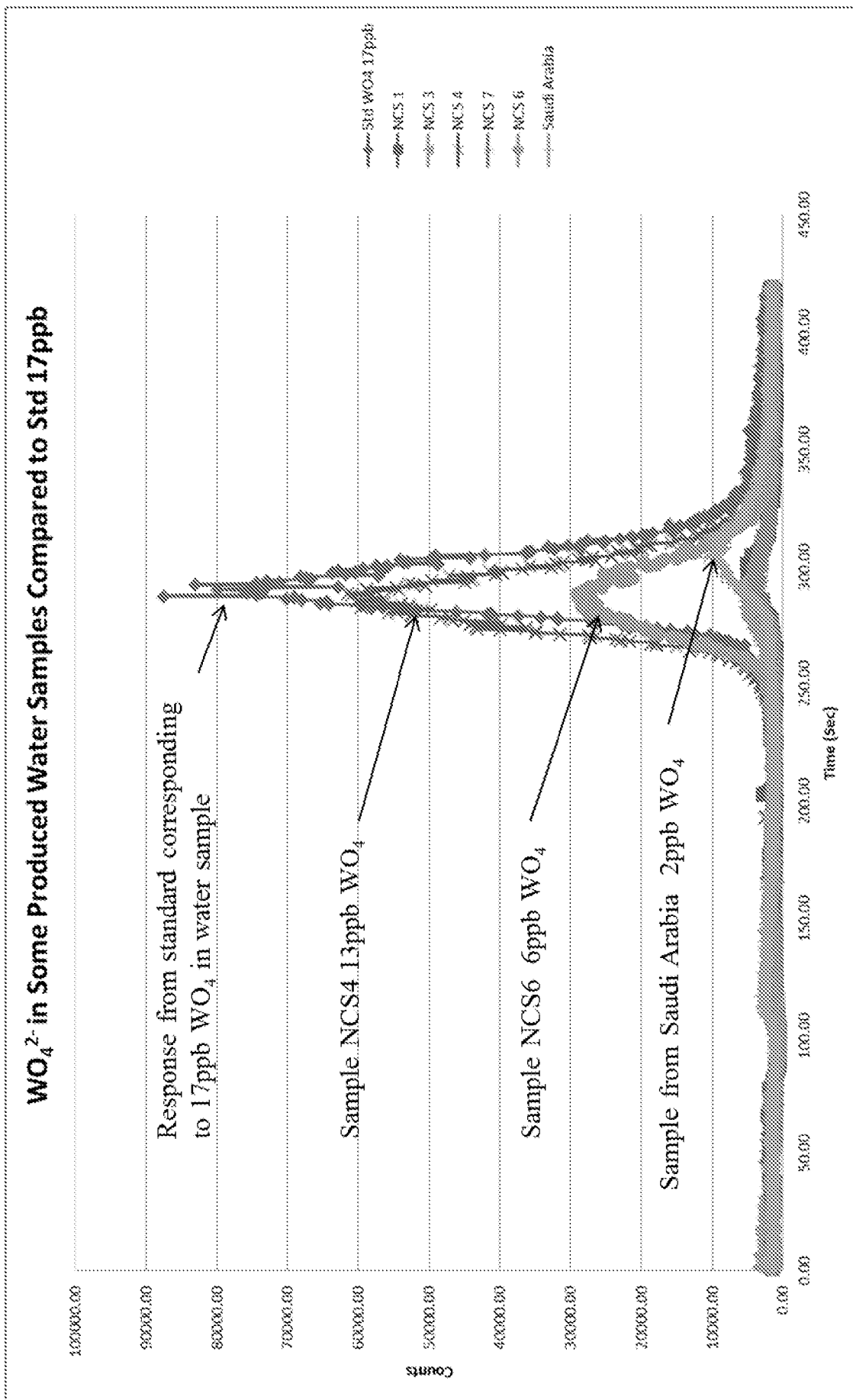


Figure 6