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(54) Title **Tracers**

(57) Abstract

The invention provides the use of at least one sparingly soluble ionic metal compound, each comprising a metal ion and at least one anion, in monitoring and/or validating the use of at least one chemical treatment agent in a subterranean reservoir. Typical compounds include oxides, sulphides, phosphates and molybdates of rare earth elements or yttrium. The inventions also provides a corresponding method for monitoring and/or validating the use of at least one chemical treatment agent in a subterranean reservoir. Tracer sources comprising at least one sparingly soluble ionic metal compound bound with a binder such as a polymer are also provided.

Tracers

Field of the invention

The present invention relates to methods for validating the effective use of scale inhibitors and tracer chemicals for use in such validation methods.

Background of the invention

The prevention of scale accumulation in petroleum wells is of great importance and scale inhibition treatments and control measures are performed regularly to maintain flow assurance. To carry out scale inhibition methods, scale inhibitor chemicals may be pumped into the reservoir, typically through the production well, and production is halted for a period so that the inhibitor can be deposited in the rock formation (e.g. by absorption or precipitation). When production is resumed, the chemicals will slowly be released from the rock and inhibit precipitation of scale in the surrounding formation and in the production tube. Scale inhibitor chemicals are designed to prevent precipitation of the most abundant types of scale found in petroleum wells (such as $BaSO_4$, $CaSO_4$, and $CaCO_3$). Sub-stoichiometric scale inhibitors can impact the formation of initial clusters from sparingly soluble salts and thereby retard the formation of crystals and delay precipitations. It is, however, difficult to verify, using existing technology, whether the scale inhibitor chemicals have been distributed along the whole production tube, or if the chemicals have reached only some zones of the well. Furthermore, in certain configurations (e.g in horizontal wells) the pressure in some parts of the well (e.g. the “heel” part close to the well head) will be lower than in other parts (e.g. the “toe” part furthest away from the well head). This potentially results in the scale inhibitor reaching only the low pressure parts such as the heel zone of the well. During current scale inhibition treatments, no monitoring of which parts of the well the scale inhibitor chemicals have reached is performed. As a result, certain areas may be treated inadequately and may accumulate scale at the expense of well performance. Alternatively, excessive scale treatments may be conducted in order to ensure that all areas are sufficiently treated. This is wasteful of both production time and materials. No methods have previously been proposed to monitor or validate the effectiveness of scale inhibitor treatment methods, particularly with regard to the areas treated. It would evidently be of considerable value to provide a method for monitoring such treatment.

The present inventors have now established that by use of appropriate tracers and conditions, a tracer system may be devised that can be used to monitor and/or validate the use of well treatment chemicals, such as scale inhibitors, in a petroleum well.

Summary of the Invention

In a first aspect, the present invention thus provides the use of a sparingly soluble ionic metal compound (each comprising a metal ion and at least one anion) in monitoring and/or validating the use of at least one chemical treatment agent in a subterranean reservoir. Such ionic metal compounds will typically be compounds which have a low solubility under the prevailing conditions of the reservoir but have an increased solubility under the conditions of the at least one chemical treatment agent.

In a further aspect, the invention also provides a method for monitoring and/or validating the use of at least one chemical treatment agent in a subterranean reservoir, with said method comprising introducing at least one sparingly soluble ionic metal compound to at least one site within said reservoir. At least one chemical treatment agent is then applied to the reservoir and at least one fluid stream produced from said reservoir is monitored for the presence and/or concentration of at least one ionic metal compound. Typically the metal ion of said at least one ionic metal compound is monitored.

Suitable sites within a reservoir may be, for example, in sand screens at one or more production layers and/or within or close to production tubes at one or more known positions. Any position on the external or internal face of the tubing, or sites at the casing, or at any part of the subterranean equipment may be used for incorporating the ionic metal compound. Other suitable sites include the insertion of the ionic metal compounds within the rock formation of the reservoir at one or more known positions. All combinations of such sites may be used, as well as other sites which will be evident to the skilled worker.

Typical ionic metal compounds appropriate for use in all aspects of the invention include salts, oxides and hydroxides of heavy metals such as rare earth metals and/or yttrium. Such compounds may particularly include molybdates, sulphides, phosphates, hydroxides and/or oxides.

Typical chemical treatment agents include scale inhibitors, many of which are well known in the art. In particular, scale inhibitors having a pH of around 7 to around 2 are highly suitable. Typically scale inhibitors may comprise at least one carboxylic acid moiety and/or at least one phosphonic acid moiety. Examples include Diethylenetriamine penta(methylphosphonic acid), Triethylenetetramine hexa(methylenephosphonic acid) and other N-phosphinomethylated poly alkylamines, phosphino polycarboxylic acids, polyacrylic acids, polymaleic acids, sulphonated polyacrylic acids and/or polyvinyl sulphonates.

Detailed Description of the Invention

Tracer technology is applied for different purposes and is frequently used for tracking fluid flow-paths and distribution in petroleum wells. One example is for monitoring in-flow of fluids to petroleum wells. Sources with different tracers can be placed along the production tube representing different production zones, and the tracer released after contact with a fluid can be identified in the produced fluids and give information on the in-flow pattern. One possibility is to insert the tracer sources under sand screens of the well. In this and other methods, the tracer can be incorporated into a polymer or another suitable matrix to allow for the controlled release over time upon exposure to the fluids. Such a system is described in patent US 6,645,769B2. Another possibility for placing the tracer sources at defined locations along the well is to use a retrofitting tool for installation in an already constructed well. The tool is used to position sleeves with a high inner diameter (so as to not significantly restrict flow) with open chambers containing tracer sources. Passing fluids are allowed to enter the chambers and release tracer compounds under certain conditions. The tracer sleeves can be fixed at defined positions along the well and be retrieved when necessary using a wireline, tractor or coiled tubing. This is a technique known to a person skilled in the art of reservoir technology, and a similar technique is described in patent US 8, 230,731B2. No known tracer method has previously been reported which can monitor or validate the use of well treatment chemicals such as scale inhibitors.

Preferred metals for use in the sparingly soluble ionic metal compound of the various aspects of the present invention are typically "rare metals". Suitable metals for use in the various aspects described herein include metals with an atomic number of 31 or greater, preferably 39 or greater. Preferably the metals chosen for use in the various aspects of the invention will have a low content of metal ions naturally present in produced water (e.g. less than 20 ng l^{-1} in the relevant produced water). Such metals include particularly the rare earth elements (especially elements of atomic number 57 to 71) and certain other useful metals such as yttrium (atomic number, Z= 39), hafnium (Z=72), niobium (Z=41), gallium (Z=31) and indium (Z=49).

Rare earth elements and Yttrium (REE and Y) can form salts, oxides and other ionic compounds that have very low solubility in water under the conditions typically found in subterranean reservoirs such as petroleum reservoirs. For instance phosphate salts of REE (especially in oxidation state 3+) are soluble in water at the 10^{-10} to 10^{-11} g/100 g range, while the solubility for most of REE and Y oxides and hydroxides ranges from 10^{-3} to 10^{-5} g/100 g, depending on the element and temperature conditions.

For use in all aspects of the present invention, the ionic metal compound will preferably have a solubility in water at 90°C and pH between 5 and 9 (e.g. pH 7) of no greater than 5×10^{-2} g/100 g, preferably no greater than 10^{-3} or 10^{-5} g/100 g (e.g. 10^{-3} to 10^{-20} g/100 g).

For use in any aspect of the present invention, the sparingly soluble ionic metal compounds may have any appropriate anion providing suitable low solubility in water (see above) and higher solubility in the presence of well treatment chemicals such as scale inhibitors. Suitable anions include oxide, hydroxide, sulphide, molybdate and phosphate ions.

The concentration of REE and Y in produced water from petroleum wells under normal production conditions will depend on the composition of the surrounding rock formation, but will usually be low and similar to that found in seawater (0.1-17 ng l^{-1}) [1,2]. However, when in contact with scale inhibitor chemicals, REE and Y salts (or oxides/hydroxides) may be dissolved to a greater extent. Without being bound by theory, it is believed that the complexing effects of the scale inhibitors serve to increase the solubility of the metal ions from the sparingly soluble salts and thus bring the salts into solution. Sparingly soluble oxides, hydroxides or salts of other rare elements, such as hafnium, niobium, gallium and indium, behave similarly. It follows that when suitable metal (e.g. REE and Y) salts, hydroxides or oxides are placed at designated locations along the production well, the concentration of the corresponding metal ions (e.g. of REE and/or Y) found in the produced water under normal production conditions will be very low, but will increase significantly in contact with treatment (e.g. scale inhibitor) chemicals. Once production has resumed following a treatment (e.g. scale inhibition), this increase in the concentration of metal ions (e.g. ions of REE and/or Y) in the produced water can be used to verify that the scale inhibition chemicals have indeed reached the intended zones along the well.

The metal ions of the ionic metal compound(s) should be detectable to a low concentration in order to provide good sensitivity without requiring large quantities to be placed in the reservoir. Typically the metal ions will be detectable down to a level of 10 ng/l in produced water, preferably down to 1 ng/l and more preferably 0.1 ng/l (or better). Detection may be by any method known in the art including, for example, mass spectrometry (e.g. inductively coupled plasma high resolution mass spectrometry).

When the dissolved metal ions (e.g. of REE and Y) have been washed out by the produced fluids, the level of the tracers (metal ions) found in the produced fluids will return to a similar level as before the (scale inhibition) treatment and further monitoring of chemical treatment will not be possible without further placement of tracers. However, the tracer particles (containing, for example the sparingly soluble ionic metal compounds) can be placed in the well in such a way that only a portion of the tracer is released each time the reservoir is treated with a well-treatment chemical (e.g. scale inhibitor), as explained in greater detail herein. In this way, the effectiveness of multiple treatments may be validated. When, for instance, a sparingly soluble ionic metal compound (e.g. REE oxide) is mixed into a polymer and exposed to a scale inhibitor, the ionic metal compound (e.g. REE oxide) in the surface layer will be dissolved, and pores in the polymer surface layer will be created. The next time that the tracer source is exposed to the scale inhibitor, the treatment chemicals will enter the pores and dissolve tracer particles (ionic metal compounds) deeper in from the polymer surface. The installed tracer sources can, therefore, be used several times to verify contact with chemicals such as scale inhibitors when treatment (scale inhibition) operations are repeated. The examples below demonstrate that the tracer source may be configured such that only a small fraction of the ionic metal compound is dissolved with each treatment. It is thus preferred that less than 50%, preferably less than 10% and more preferably less than 1%, of the ionic metal compound is dissolved when a single well treatment with a well treatment chemical (as described herein) is employed.

In the patent US 8,230,731B2, a technique for the detection of water incursion in a petroleum production well using several tracer compounds, including lanthanides, is described. The use of lanthanides and other rare elements for the monitoring of the in-flow of fluids in petroleum production wells is described in the patent WO 2007/102023A1. A third patent where lanthanide compounds are used as tracers is US 4,755,469A, where the tagging oil with lanthanide metal salts of fatty acids is described for various purposes such as oil flow monitoring and the identification of an oil spill. None of these documents relate to the use of well treatment chemicals or the monitoring of well treatments (e.g. scale inhibition) by the use of tracers. The present invention differs from the above mentioned patents in that it provides a method for the verification that scale inhibitor chemicals have reached the intended zones in a petroleum production well.

In the present invention, the ionic metal compounds are typically placed at sites of interest in the subterranean reservoir (e.g. petroleum reservoir). Where more than one ionic metal compound is used, these will generally comprise different metal ions and will be placed at separate positions in the reservoir, preferably at different production layers. At least one ionic metal compound will be employed in the uses and methods of the invention and this may be at least two (e.g. 2 to 10 or 2 to 20) different metal compounds, each comprising ions of a different metal or different isotope.

Typically, the ionic compounds used in the various aspects of the present invention will comprise a metal ion having natural isotopic abundance. However, in one embodiment of the invention suitable for application to all aspects described herein, the ionic compound may comprise at least one metal isotope at greater than its natural abundance. Such isotopes will typically be non-radioactive (stable) isotopes. Different isotopes may be distinguished by detection methods such as the mass-spectroscopic methods described herein. Thus, where “different metals” or “different metal ions” are referred to herein, these may be chemically different elements or may be different isotopes of the same chemical element (or a combination of different elements and different isotopes) where context allows. Isotopic labeling allows for a much greater diversity of labels but will potentially be more expensive than labeling with different metal elements and so will preferably be used where a sufficient number of different suitable metal elements are not available.

Obviously, where the detection sensitivity is sufficient, mixtures of isotopes may be used, provided that the ions originating from different sites can be distinguished. For example, if a metal has a common isotope of atomic mass Z and rare isotopes Z+1 and Z+2, salts having mostly Z with a low percentage Z+1 can be distinguished from salts having mostly Z and a low percentage Z+2, providing sufficient detection sensitivity is possible. It may be more economical to apply a larger quantity of a material with a slight isotopic enhancement than to apply a small amount of material of high isotopic purity. Thus, isotopic labeling may be carried out by enhancing at least one isotope by at least 1% above its natural abundance, preferably at least 5% and more preferably at least 10% (e.g. 10 to 99%) above its natural abundance.

Tracer sources (such as polymer rods) containing sparingly soluble metal (e.g. REE and/or Y) salts (e.g. oxides) can be placed at known positions in a reservoir using well known methods. For example, the tracers may be placed under sand screens during the construction of a new well or be placed in chambers in sleeves inserted into an existing production well using a tool that is operated from the well head. Several such sources (e.g. treated sand screens or sleeves), each containing different tracer(s) can be located in different zones along the production well. The ionic metal compounds (e.g. REE or Y salts or oxides) are sparingly soluble under normal production conditions giving rise to low background concentrations of metal ions (e.g. REE and/or Y ions) in the produced waters. When in contact with scale inhibition chemicals, the dissolution of the metal (e.g. REE and/or Y) salts will increase significantly, resulting in an increased concentration of metal ions in the produced water when production is resumed. Where the presence of a metal ion at above background level is detected, this indicates that the well treatment chemical (e.g. scale inhibitor) reached the site of the tracer which comprises that metal. Thus, the actual distribution of the scale inhibition chemicals along the well can be verified by analysis of the produced water and comparison of measured metal ions with known sites of ionic metal compound tracers.

The sparingly soluble tracers can be mixed into a polymer, but can also be present in other forms. Where the sparingly soluble ionic compound is mixed with an inert material such as a polymer, ceramic or glass, the inert material will typically be little changed by exposure to the reservoir environment and the ionic compound will dissolve little in formation water. However, when the reservoir is treated with at least one chemical treatment agent such as a scale inhibitor, the ionic material will be partially dissolved and produced from the well. This will create pores in the inert material allowing subsequent treatment chemicals to access deeper into the material and dissolve more of the sparingly soluble compound. The application of poly methyl methacrylate (PMMA) is described in the examples below, but many different types of polymers can be employed, for instance epoxy resins, melamine-formaldehyde resins, among others. The tracers may also be present as layers of sintered salts or oxides on the surface of ceramic materials or metals, or mixed into such materials. REE and Y salts are exemplified below, but sparingly soluble salts of other rare elements such as hafnium, niobium, gallium and indium are expected to function equally as well.

Tracer sources comprising at least one a sparingly soluble ionic metal compound mixed and solidified with at least one polymer or ceramic material comprise a further aspect of the present invention.

The tracer sources of the present invention comprise at least one least one a sparingly soluble ionic metal compound as described herein, bound with at least one polymer or ceramic material. Suitable materials will be well known to the skilled worker and include polymer, ceramic materials and glass materials such as those described herein. Preferred sparingly soluble ionic metal compounds for all aspects of the present invention, particularly the tracer sources include oxides, sulphides, phosphates and molybdates, particularly of rare earth elements (REEs) or yttrium (Y). Oxides of Eu, Pr and Gd are particularly appropriate, such as Eu_2O_3,Pr_2O_3 and/or Gd_2O_3. The tracer sources will be bound into rods, sheets, blocks, rings, spheres, spheroids, tubes, liners or any shape suitable for application to the reservoir. The binding material will typically be a material that is insoluble in the formation fluids such as PMMA, epoxy resins, melamine-formaldehyde resins or any suitable ceramic or glass material including silica, titania, alumina and mixtures thereof.

In the present invention the use of sparingly soluble ionic metal compounds (e.g. REE and/or Y salts or oxides) as tracers for the verification that scale inhibitor chemicals have reached intended zones in a reservoir is described. Tracer sources of at least one, preferably at least two (e.g. 2 to 10) sparingly soluble ionic metal compounds (e.g. REE and/or Y salts or oxides) are located in different zones of a petroleum production well, and when treatment chemicals (e.g. scale inhibitor solutions) are pumped into the well, the verification of its contact with the different zones of the well can be achieved. The sparingly soluble ionic metal compounds are gradually dissolved by the scale inhibitor chemicals and the amounts of metal ions (e.g . ions of REE and/or Y elements) in the produced water samples collected from the well head are determined when production is resumed.

Many sparingly soluble ionic metal compounds, such as oxides, hydroxides and sulfides of rare elements will be more soluble at low pH than at pH 6-8 normally found in produced water. The present invention may therefore also be used to verify that chemicals used in acid treatment of a well have reached the intended zones. The ionic metal compound (e.g. rare element) tracers are for this application limited to acid soluble compounds (e.g. those having a solubility in water at pH 2 of greater than $5\ 10^{-2}$g / 100g, preferably at least 0.1 g/100g, such as 0.2 to 20 g/100g) such as oxides, hydroxides or sulfides.

Other oil field chemicals used may include corrosion inhibitors, chemicals to inhibit deposition of wax, asphaltenes or naphthenates. The verification that oil field chemicals other than scale inhibitors and/or acids have reached the intended zones may be achieved by co-introduction into the reservoir with a scale inhibitor, chelator or acid treatment compound that dissolves the tracers – the chemical and scale inhibitor, acid treatment compound and/or chelator are injected at the same time - , or injection of scale inhibitor, acid treatment compound and/or chelator could follow injection of the main oil field chemical. As used herein, the term “chemical treatment agent” therefore includes single agents, such as scale inhibitors and/or acid treatment chemicals. These will typically serve in themselves to solubilize the sparingly soluble ionic compounds referred to herein. Additionally or alternatively, the chemical treatment agents may comprise at least a portion of at least one scale inhibitor, acid and/or chelating compound. This second chemical agent serves to “tag” the first agent by solubilizing the ionic compounds and therefore allowing the presence of the mixture in the region of the ionic compound to be validated. Acids and chelating agents are well known in the art and include mineral acids and organic acids, mono- di- and/or multi-dentate chelators and similar compounds. The chemical treatment agent may comprise a primary treatment agent (such as corrosion inhibitors, chemicals to inhibit deposition of wax, asphaltenes and/or naphthenates) and a secondary chemical treatment agent (such as an acid, chelating agent and/or scale inhibitor). In this embodiment (applicable to all aspects of the invention), the secondary agent will typically be present at less than 50% (e.g. 0.1% to 50% or 1 to 25%) of the concentration of the primary chemical treatment agent. The preferred ionic compounds and tracer sources will be those described herein in all aspects.

Brief description of drawings

Figure 1 is a graph showing a plot of the concentration of Pr and Er versus the accumulated elution volumes of collected fractions from leaching experiments with poly methyl methacrylate (PMMA) rods containing 30% (w/w) Pr_2O_3 and Er_2O_3 at 70°C. The rods were leached with artificial formation water (pH 7), scale inhibitor solution (pH 3.9) and formation water respectively.

Figure 2 is a graph showing a plot of the accumulated concentration of Eu, Pr and Gd versus time of sampling after the start of the first flow-rig leaching experiment with PMMA rods containing 12.5% (w/w) Eu_2O_3, 6.3% Pr_2O_3 and 6.3% Gd_2O_3 at 80°C. The rods were first leached with tap water and then with scale inhibitor solution (pH 6.9).

Figure 3 is a graph showing a plot of the accumulated concentration of Eu, Pr and Gd versus time of sampling after the start of the second flow-rig leaching experiment with PMMA rods containing 12.5% (w/w) Eu_2O_3, 6.3% Pr_2O_3 and 6.3% Gd_2O_3 at 80°C. The rods were first leached with tap water and then with scale inhibitor solution (pH 6.9).

Examples

Example 1

The REE oxides Pr_2O_3 and Er_2O_3 were mixed into PMMA at a concentration of 30% by weight and molded into each of two rods of size 3x8x75 mm. The rods were installed in a glass column and the void volume was filled up with 3mm glass beads. Artificial formation water equivalent to formation water from the Gullfaks field on the Norwegian continental shelf was pumped through the column at a flow rate of 0.5 ml/min. The temperature was kept at 70°C throughout the experiment. The eluted water was collected in fractions at volumes ranging from 30 to 760 ml, and the concentration of Pr and Er were analyzed using inductively coupled plasma high resolution mass spectrometry (HR-ICP-MS). After nearly 6 days (4300 ml) of formation water flow, the eluent was changed to a scale inhibitor solution with a pH of 3.9. This scale inhibitor solution was pumped through the column for a period of 5 hours. The Pr concentration leached by the flow of fluid increased from a mean concentration of 76 ng/ml (with formation water) to a peak value 6.2 mg/ml (with scale inhibitor solution). The corresponding values for the Er concentration were 83 ng/ml and 8.8 mg/ml respectively. The concentration of Pr and Er then returned to near pre-inhibitor concentrations when the column was once again eluted with the formation water. An increase in eluted Pr and Er concentration by a factor of approximately 100 was thus achieved when the REE oxides Pr_2O_3 and Er_2O_3 were in contact with the scale inhibitor. A plot of the results from the leaching experiment is shown in Figure 1. Of the total amount of 0.5g Eu_2O_3 present in the rod, only about 0.8mg (approx. 0.16%) was leached out during the experiment. Repeated treatment with scale inhibitors would thus be expected to yield further peaks in metal ion concentration.

Example 2

A flow rig was used in the following experiment, consisting of a 4 m long steel tube with inner diameter 72 mm connected to a casing within which a 2 m long tool was installed. The tool consists of chambers for installing up to 30 tracer rods and the chambers have openings to allow for fluid to enter and come in contact with the tracer rods. The inner diameter of the tool is 145 mm, and the volume of the flow rig is calculated to be approximately 50 liters. Tracer rods with a size of 9x28x500 mm were placed in the tool beforehand, each containing different REE oxides. The tracer rods were made by mixing 10 to 20 g of rare earth oxide powder (Eu_2O_3, Pr_2O_3 and Gd_2O_3) into a PMMA polymer before hardening. The flow rig was connected to a reservoir filled with 1000 liters of tap water which was circulated at a flow rate of 490 L/min and a constant temperature of 80^{o}C. The total volume of fluid in the system was, therefore, 1050 liters during the tap water circulation period which extended to 3 hours and 20 minutes during the first leaching experiment. Samples of the circulating tap water were taken at approximately 1 hour intervals and analyzed for their concentration of REE (Eu, Pr and Gd) using HR-ICP-MS. The concentration of Eu in the circulating tap water was found to be 50 pg/ml at the start of the experiment and 100 pg/ml after 3 hours and 20 minutes. Once a volume corresponding to the total volume of the fluid in the flow rig had passed over the tracer rods 93 times (98 m^3), a scale inhibitor solution with a pH of 6.9 was pumped from a 250 liter reservoir and circulated through the flow rig. Samples of the scale inhibitor solution were collected at intervals of approximately 10 minutes and analyzed for REE concentration. The results from the leaching experiment with rods containing Eu_2O_3, Pr_2O_3 and Gd_2O_3 are plotted in Figure 2. The higher concentration of Eu observed in the circulated scale inhibitor solution compared to Pr and Gd is due to the higher concentration of Eu_2O_3 in the tracer rods. The concentration of Pr_2O_3 and Gd_2O_3 was 6.5% (w/w), while the concentration of Eu_2O_3 was 12.5%. Already after 2 minutes of circulation with scale inhibitor or when a volume of twice the total volume in the rig had been exposed to the tracer rods, a significant increase in the concentration of REE was observed. After about 50 minutes, or 80 circulations of scale inhibitor solution, the concentration of Eu leached had increased to around 100 ng/ml, approximately 1000 times higher than that observed in the tap water. The flow rig was then flushed with tap water and a second leaching experiment was completed. The results from the second leaching experiment are shown in Figure 3. The total amount of Eu_2O_3 dissolved by the scale inhibitor solution during the two leaching experiments was calculated as 22.5 mg, corresponding to 0.11% of the total amount of Eu_2O_3 (20 g) molded into the tracer rod.

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Claims:

1) Use of at least one sparingly soluble ionic metal compound, each comprising a metal ion and at least one anion, in monitoring and/or validating the use of at least one chemical treatment agent in a subterranean reservoir.

2) Use as claimed in claim 1 wherein the sparingly soluble ionic metal compound is a salt, oxide or hydroxide of a metal having atomic number of 31 or greater.

3) Use as claimed in any preceding claim wherein the sparingly soluble ionic metal compound is a salt, oxide or hydroxide of a metal selected from the rare earth elements, yttrium, hafnium, niobium, gallium and indium.

4) Use as claimed in any preceding claim wherein the chemical treatment agent is a scale inhibitor.

5) Use as claimed in any preceding claim wherein the chemical treatment agent is a scale inhibitor comprising at least one carboxylic acid moiety and/or at least one phosphonic acid moiety.

6) Use as claimed in any preceding claim wherein the sparingly soluble ionic metal compound has a solubility in water at 50°C and pH 7 of no greater than 5×10^{-2} g/100 g.

7) A method for monitoring and/or validating the use of at least one chemical treatment agent in a subterranean reservoir, said method comprising;

i) introducing at least one sparingly soluble ionic metal compound, each compound comprising a metal ion and at least one anion, to at least one site within said reservoir,

ii) applying said at least one chemical treatment agent; and

iii) monitoring at least one fluid stream produced from said reservoir for the presence and/or concentration of at least one metal ion comprised in said at least one ionic metal compound.

8) The method of claim 7 wherein said at least one metal ion is detectable in produced water down to a level of at least 10 ng/l.

9) The method of claim 7 or claim 8 wherein said ionic metal compound is dissolved to no more than 10% by a single treatment of the reservoir with a chemical treatment agent.

10) The method of any of claims 7 to 9 wherein at least two sparingly soluble ionic metal compounds comprising different metal ions are placed in two separate positions in said reservoir.

11) The method of any of claims 7 to 10 wherein said metal compound is placed in the form of a tracer source comprising said compound and at least one polymer.

12) The method of any of claims 7 to 11 wherein said metal compound is placed in a sand screen and/or in an annular ring within a production pipe.

13) The method of any of claims 7 to 12 wherein the chemical treatment agent comprises at least one scale inhibitor, acid and/or chelator.

14) The method of any of claims 7 to 13 wherein the chemical treatment agent comprises a primary treatment agent and a secondary treatment agent, wherein the secondary treatment agent is at least one selected from a scale inhibitor, an acid, a chelator and mixtures thereof.

15) A tracer source comprising a sparingly soluble ionic metal compound and at least one polymer.

Figures

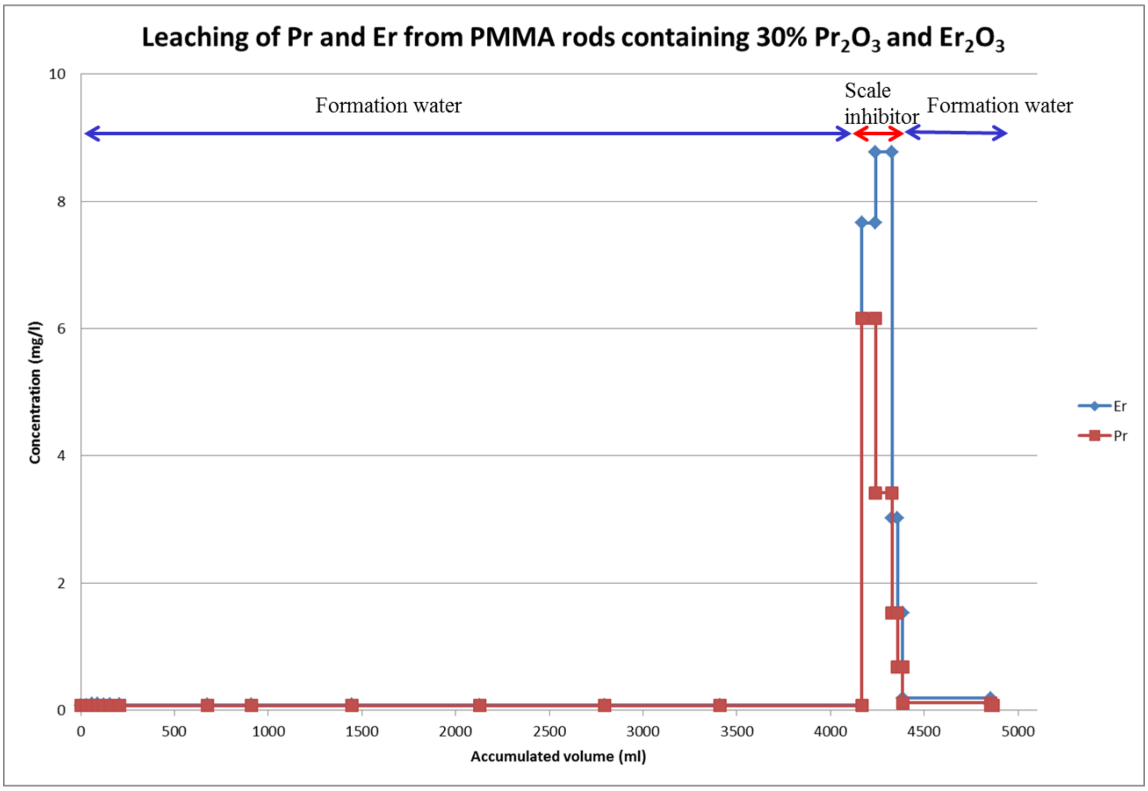

Figure 1

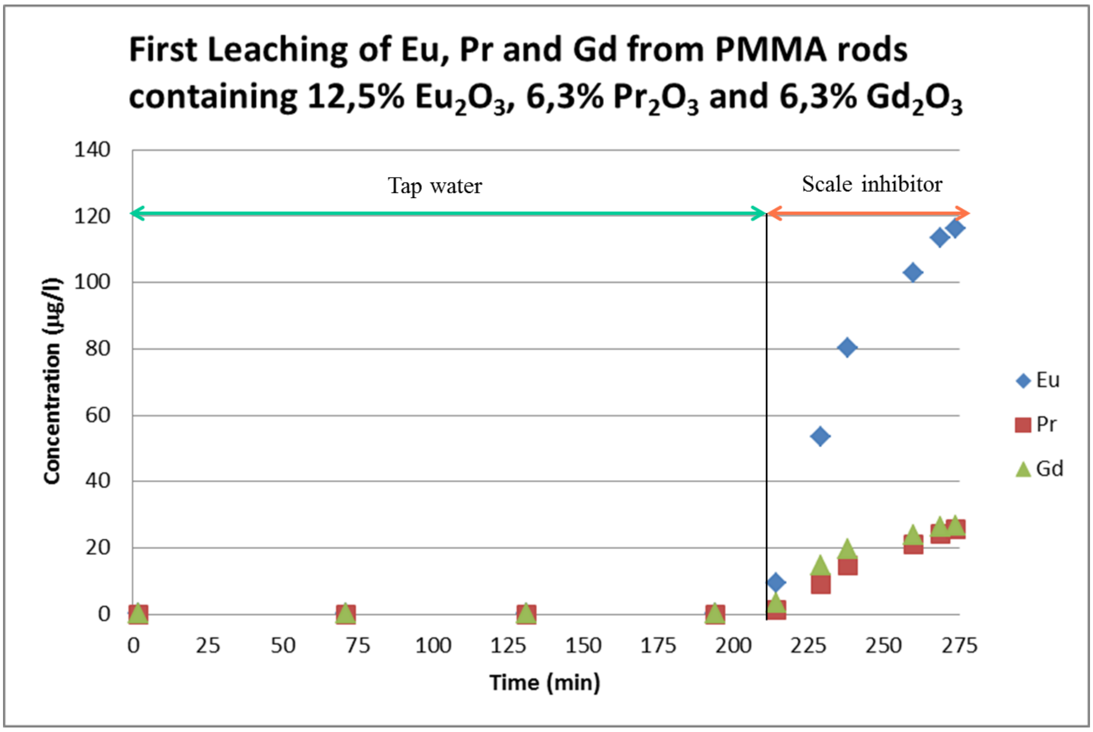

Figure 2

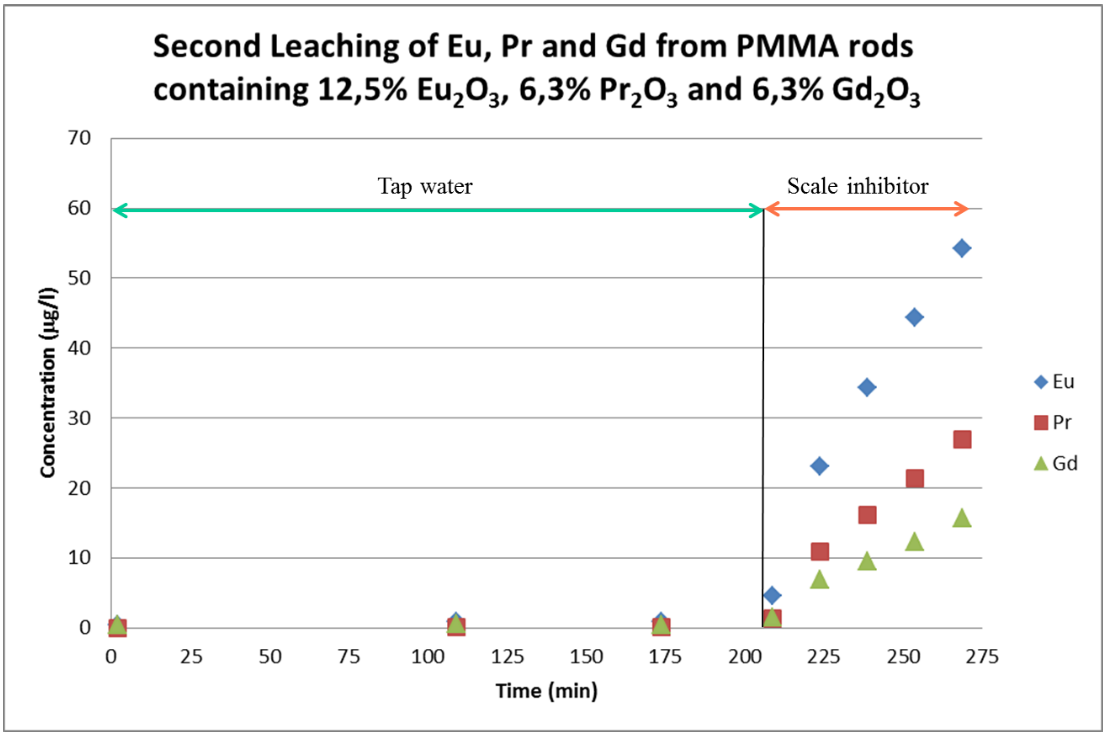
Second Leaching of Eu, Pr and Gd from PMMA rods containing 12,5% Eu_2O_3, 6,3% Pr_2O_3 and 6,3% Gd_2O_3
Tap water
Scale inhibitor
Concentration (µg/l)
70
60
50
40
30
20
10
0
0
25
50
75
100
125
150
175
200
225
250
275
Time (min)
Eu
Pr
Gd

Figure 3