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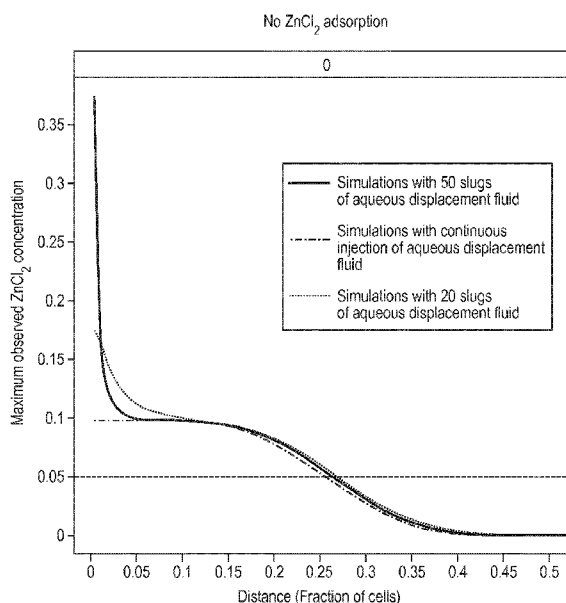


FIG. 1a

(57) Abstract: A method for recovering crude oil from a reservoir comprising injecting into an oil-bearing reservoir alternating slugs of an aqueous displacement fluid comprising an aqueous solution of zinc chloride or zinc bromide and of an aqueous spacer fluid characterized in that: a) the pH of each of the slugs of aqueous displacement fluid is less than 5.5 and the pH of each of the slugs of aqueous spacer fluid is less than 8.5; b) the number of injected slugs of aqueous displacement fluid, n , is in the range of 15 to 1000 per swept pore volume, PVR; c) the injected pore volume of each individual slug, $PV_{\text{slug-}i}$, of aqueous displacement fluid is in the range of 10^{-12} to 10^{-2} of the PVR; d) the total injected pore volume of the slugs of aqueous displacement fluid is in the range of 10^{-8} to 10^{-1} of the PVR; e) the injected pore volume of each individual slug of aqueous spacer

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fluid, $PV_{\text{spacer-}i}$ is in the range of 0.0001 to 0.1000 of the PVR; f) the total injected pore volume of the slugs of aqueous spacer fluid is in the range of 0.9000000 to 0.9999999 of the PVR; g) the reservoir rock has a dispersivity, α , in the range of 1 to 30; and 20 h) the quantity of zinc delivered to the reservoir by the plurality of slugs of aqueous displacement fluid is equal to or greater than a predetermined minimum quantity (MQ).

OIL RECOVERY METHOD

Technical Field

The present invention relates to a method for injecting an aqueous solution of a zinc
5 halide salt into a reservoir for recovery of crude oil therefrom.

Background

It has long been known that only a portion of the oil can be recovered from an oil-
bearing reservoir as a result of the natural energy of the reservoir. So-called secondary
recovery techniques are used to recover additional oil from a reservoir, the simplest
10 method of which is by direct replacement with another medium, usually water or gas.

International Patent Application Publication No. WO 2015/007749 relates to a
method for recovering crude oil from a reservoir that is penetrated by at least one injection
well, the method comprising: injecting an aqueous displacement fluid comprising a
solution of a zinc salt in an aqueous base fluid into the reservoir from the injection well
15 wherein the aqueous base fluid has a total dissolved solids (TDS) concentration in the
range of 200 to 250,000 ppmv, and a viscosity in the range of 1.00 to 2.00 centipoise (cP)
at standard temperature and pressure; and wherein the aqueous displacement fluid has a
dissolved zinc concentration in the range of 10 to 3,750 ppmv. WO 2015/007749 also
teaches that the aqueous displacement fluid may be injected into the reservoir either
20 continuously or in the form of a slug of controlled pore volume (PV).

International Patent Application Publication No. WO 2015/007749 also teaches that
the form in which the dissolved zinc exists in aqueous solution either prior to injection into
the reservoir or within the reservoir may be dependent on pH. Typically, the risk of
precipitation of insoluble zinc salts is mitigated at acidic pH. Accordingly, WO
25 2015/007749 teaches that an acid may be added to the aqueous base fluid either before or
after the addition of the zinc salt. Alternatively, the acid and zinc salt may be added
simultaneously to the aqueous base fluid. Addition of an acid to the aqueous displacement
fluid of WO 2015/007749 is also said to mitigate the risk of precipitation of insoluble zinc
hydroxide, $[Zn(OH)_2]$. It would be advantageous to eliminate the requirement for adjusting
30 the pH of the aqueous displacement fluid with an acid and the associated costs of
purchasing and transporting acid to the injection site.

Summary

According to the present invention there is provided a method for recovering crude oil from a reservoir comprising at least one layer of reservoir rock having crude oil and a formation water within the pore space thereof wherein the layer(s) of reservoir rock is penetrated by at least one injection well and at least one production well, the method comprising:

injecting into the layer(s) of reservoir rock from the injection well, alternating slugs of an aqueous displacement fluid comprising an aqueous solution of a zinc halide salt selected from zinc chloride, zinc bromide and mixtures thereof and of an aqueous spacer fluid characterized in that:

- (a) the pH of each of the slugs of aqueous displacement fluid is less than 5.5 and the pH of each of the slugs of aqueous spacer fluid is less than 8.5;
- (b) the number of injected slugs of aqueous displacement fluid, n , is in the range of 15 to 1000 per swept pore volume, PVR , of the layer(s) of reservoir rock;
- (c) the injected pore volume of each individual slug, PV_{Slug-i} , of aqueous displacement fluid is in the range of 10^{-12} to 10^{-2} of the swept pore volume, PVR , of the layer(s) of reservoir rock:

$$10^{-12} \leq PV_{Slug-i} \leq 10^{-2};$$

- (d) the total injected pore volume of the slugs of aqueous displacement fluid is in the range of 10^{-8} to 10^{-1} of the swept pore volume, PVR , of the layer(s) of reservoir rock:

$$10^{-8} \leq \sum_{i=1}^n PV_{Slug-i} \leq 10^{-1};$$

- (e) the injected pore volume of each individual slug of aqueous spacer fluid, $PV_{Spacer-i}$, is in the range of 0.0001 to 0.1000 of the swept pore volume, PVR , of the layer(s) of reservoir rock:

$$0.0001 \leq PV_{Spacer-i} \leq 0.1000;$$

- (f) the total injected pore volume of the slugs of aqueous spacer fluid is in the range of 0.9000000 to 0.9999999 of the swept pore volume, PVR , of the layer(s) of reservoir rock;

$$0.9000000 \leq \sum_{i=1}^n PV_{Spacer-i} \leq 0.9999999;$$

- (g) the reservoir rock has a dispersivity, α , in the range of 1 to 30% of the interwell distance between the injection well and production well; and

- (h) the quantity of zinc delivered to the layer(s) of reservoir rock by the plurality of slugs of aqueous displacement fluid is equal to or greater than a predetermined minimum quantity (MQ).

Suitably, the minimum quantity of zinc, MQ , delivered to the layer(s) of reservoir rock by injecting the plurality of slugs of aqueous displacement fluid may be determined using Equation 1 below:

$$MQ = \left[C_{InjAvg} \cdot (4\sqrt{\alpha} \operatorname{erf}^{-1} \left\{ \frac{C_T}{C_{InjAvg}} \right\}) + RAC \right] \cdot PVR \quad (1)$$

wherein RAC is the adsorption capacity of the reservoir (hereinafter “Reservoir Adsorption Capacity”), C_T is the threshold concentration for zinc, C_{InjAvg} is the initial average concentration of zinc for the injected alternating slugs (*i.e.*, averaged across the slugs of aqueous spacer fluid and the aqueous spacer slugs), α is the dispersivity of the reservoir and PVR is the swept pore volume of the layer(s) of reservoir rock.

Suitably, C_{InjAvg} is determined using Equation 2 below:

$$C_{InjAvg} = \frac{\sum_{i=1}^n (C_{slug-i} \cdot PV_{slug-i})}{\sum_{i=1}^n (PV_{slug-i} + PV_{spacer-i})} \quad (2)$$

wherein C_{slug-i} is an initial concentration of zinc in an individual slug of aqueous displacement fluid.

The person skilled in the art will understand that, in the method of the present invention, alternating slugs of aqueous displacement fluid and aqueous spacer fluid are injected into the layer(s) of reservoir rock from the injection well and produced fluids comprising oil, water and gas are removed from the production well.

Definitions

“Aqueous drive fluid” is an aqueous fluid that may be injected into an injection well after injection of the final slug of the alternating slugs of aqueous displacement fluid and aqueous spacer fluid.

“Bank of oil” is a term well known to the person skilled in the art and refers to a portion of the layer(s) or reservoir rock where the oil saturation is increased because of the application of an enhanced oil recovery process that targets immobile oil.

“Dispersivity” of a layer of reservoir rock, α , is the dispersivity in the direction of flow (also referred to as “longitudinal dispersivity”). Dispersivity is a characteristic property of reservoir rock arising from velocity differences within pores on a microscopic scale and path differences due to the tortuosity of the pore network of the reservoir rock.

Dispersivity is related to the dispersion coefficient, D , of a porous medium and the advective flow velocity, v , of a fluid through the reservoir rock as follows:

$$D = \alpha \cdot v$$

wherein α has units of length (typically metres). Dispersivity for a layer of reservoir rock

5 may also be expressed as a dimensionless number. For example, a dimensionless dispersivity may be determined as a percentage of the system length (in particular, as a percentage of the length of a core plug taken from the reservoir rock, or as a percentage of an interwell distance between a pair of injection and production wells that penetrate the layer(s) of reservoir rock). Alternatively, the dimensionless dispersivity may be defined as
10 a percentage of the distance travelled (for example, as a percentage of the distance that an injection fluid has travelled from an injection well to a production well).

In Equation 1, “erf” is an error function.

“Formation water” is the water associated with the reservoir rock, i.e., connate water, any invading aquifer water and any previously injected water.

15 “Initial concentration of zinc” is the concentration of zinc in the aqueous displacement fluid prior to injection of the slugs of aqueous displacement fluid into the injection well. Typically, the initial concentration of zinc has the units of mg/L or mol/L. It is to be understood that the initial concentration of zinc takes into account the background concentration of any naturally occurring zinc in the water used as solvent for
20 the aqueous displacement fluid.

“Incremental oil production” means an amount of produced oil that is at least 1%, preferably at least 3%, more preferably, at least 5%, in particular, at least 7.5%, for example, at least 10% above that achieved or predicted to be achieved when waterflooding the reservoir with the injection water used as the aqueous spacer fluid in the absence of a
25 zinc halide salt additive.

“Predicted incremental oil production” means an amount of incremental oil determined from coreflood experiments or Single Well Chemical Tracer (SWCT) tests which are techniques well known to the person skilled in the art.

30 “Injection site” is the site at which the alternating slugs of aqueous displacement fluid and aqueous spacer fluid are injected into the injection system of the injection well.

“Injection temperature and pressure” is the temperature and pressure in the injection well adjacent the layer(s) of reservoir rock into which the aqueous displacement

fluid is to be injected.

“Natural pH of the aqueous displacement fluid” is the pH of the aqueous displacement fluid in the absence of any added acid or added base.

“Swept pore volume (PVR)” is the pore volume of the layer(s) of reservoir rock swept by injected fluids (slugs of aqueous displacement fluid, aqueous spacer slugs and any aqueous drive fluid) between an injection well and a production well, averaged over all flow paths between the injection well and production well. Where an injection well has two or more associated production wells, the term “swept pore volume” means the pore volume of the layer(s) of reservoir rock swept by the injected fluids between the injection well and its associated production wells.

The values of pore volumes given for the slugs of aqueous displacement fluid and for the slugs of aqueous spacer fluid are based on the swept pore volume (PVR) of the layer(s) of reservoir rock. The pore volumes refer to the injected pore volumes of the slugs prior to dispersion within the layer(s) of reservoir rock.

PV_{Slug-i} is the pore volume of an individual slug of aqueous displacement fluid.

$PV_{Spacer-i}$ is the pore volume of an individual slug of aqueous spacer fluid.

C_{InjAvg} is the average initial concentration of zinc in the alternating sequence of slugs of aqueous displacement fluid and of aqueous spacer fluid and typically has units of mg/L or mol/L.

C_{Slug-i} is the initial concentration of zinc in an individual slug of aqueous displacement fluid.

$C_{Spacer-i}$ is the initial concentration of zinc in an individual slug of aqueous spacer fluid and, for aqueous spacer fluids having a low background concentration of zinc (for example of less than 1 ppm), may be taken to be zero. Therefore, $C_{Spacer-i}$ is not typically included in Equation 2. However, the person skilled in the art would understand that if the aqueous spacer fluid has a relatively high background concentration of zinc, Equation 2 may be expanded to include $C_{Spacer-i}$.

“Threshold concentration, C_T , for zinc” is the minimum initial concentration of zinc in the aqueous displacement fluid predicted to achieve incremental oil production upon continuous injection of one pore volume of aqueous displacement fluid into the reservoir followed by injection of an aqueous drive fluid. Typically, C_T has units of mg/L or mol/L. It is to be understood that the threshold concentration takes into account the natural

background concentration of any zinc in the water used as solvent for the aqueous displacement fluid.

“Minimum Quantity of zinc (*MQ*)” is the minimum quantity (or amount) of zinc delivered to the at least one layer of reservoir rock by the slugs of aqueous displacement fluid and typically has units of mass (for example, mg) or mol. It is to be understood that the *MQ* of zinc also takes into account the natural background concentration of any zinc in the water used as solvent for the aqueous displacement fluid.

“Reservoir Adsorption Capacity (*RAC*)” is the amount of zinc adsorbed by the reservoir and typically has the units mg/L of accessible pore volume or mol/L of accessible pore volume.

The person skilled in the art would understand that the units for C_{InjAvg} , C_{Slug-i} , C_T , *MQ* and *RAC* should be consistent (based either on mass of zinc or moles of zinc).

“Travel distance” means the distance travelled by the front of the dispersively mixed fluids (and hence the front of zinc) through the layer(s) of reservoir rock from the injection well towards the production well. The unit “ppmv” is “parts per million on a volume of water basis” and is equivalent to the unit “mg/L”.

Detailed Description

In the method of the present invention, alternating slugs of the aqueous displacement fluid and of the aqueous spacer fluid are injected into the layer(s) of reservoir rock to release oil from the reservoir rock and to produce fluids comprising oil, water and gas from the production well. As discussed in more detail below, there may be more than one injection well and more than one production well.

Injection of the alternating slugs may commence with either a slug of aqueous displacement fluid or a slug of aqueous spacer fluid. Similarly, injection of the alternating slugs may terminate with either a slug of aqueous displacement fluid or a slug of aqueous spacer fluid. Generally, an aqueous drive fluid is injected into the layer(s) of reservoir after injecting the final slug of the alternating series of slugs to sweep the dispersively mixed fluids (and hence the bank of released oil) towards a production well.

The alternating slugs of aqueous displacement fluid and of aqueous spacer fluid are believed to mix within the reservoir with the extent of mixing being dependent upon the dispersivity of the reservoir rock and the travel distance of the front of zinc. Typically, the dispersivity of a layer of reservoir rock is in the range of 1 to 30%, preferably 2 to 15%,

more preferably, 2 to 10% of the interwell distance or the travelled length. The dispersivity of the layer(s) of reservoir rock into which the aqueous displacement fluid is to be injected may be determined from dispersivity tests performed on samples of a reservoir rock or may be determined from a single well chemical tracer test performed on a well that
5 penetrates the oil-bearing layer(s) of reservoir rock. When the dispersivity tests are performed on samples of a reservoir rock, the dispersivity tests are typically performed during coreflood experiments.

Suitably, the aqueous displacement fluid is delivered to the injection site as an aqueous concentrate having a concentration of zinc halide salt (selected from zinc chloride, zinc bromide, and mixtures thereof, preferably, zinc chloride) of at least 10% by weight,
10 preferably, at least 20% by weight. The upper limit for the concentration of zinc halide salt in the concentrate is the saturation concentration of zinc halide salt at the ambient conditions encountered at the injection site. Suitably, the concentration of zinc halide salt is in the range of 10 to 75% by weight, preferably, 20 to 70% by weight, more preferably,
15 30 to 60%, for example, 40 to 55% by weight. Suitably, the solvent for the concentrate is selected from fresh water, potable water, distilled water or deionized water.

Without wishing to be bound by any theory, it is believed that zinc bromide species are less active than zinc chloride species in releasing incremental oil from the reservoir rock. It is therefore preferred that the concentrate comprises from 0 to 10 mole%, more
20 preferably from 0 to 5 mole%, in particular, from 0 to 2 mole% of the zinc bromide (based on the total molar amount of zinc chloride and any zinc bromide in the aqueous concentrate). Preferably, the concentrate contains only zinc chloride (100 mole% zinc chloride).

The concentrate may be supplied to the injection site for the reservoir at the desired
25 initial zinc concentration and at the desired pH of less than 5.5 and may be injected directly into the layer(s) of reservoir rock without further dilution into an injection water. Thus, the concentrate may serve as the aqueous displacement fluid. This has the advantage of eliminating the requirement to deliver an acid to the injection site. Typically, the concentration of zinc halide in the concentrate is selected such that the concentrate has a
30 natural pH of below 5.5, preferably, below 5.0, yet more preferably below 4.5, in particular, below 4.0, thereby also eliminating the requirement for adjusting the pH of the concentrate with an acid at its production site.

The pore volume sizes of the plurality of slugs of concentrate in the alternating sequence of slugs may be the same or different. Typically, an injection water, available at the injection site, serves as the aqueous spacer fluid. The pore volume sizes of the plurality of aqueous spacer slugs in the alternating sequence of slugs may be the same or different.

5 Injection of alternating slugs of the concentrate and of aqueous spacer fluid may continue until the desired total pore volume of concentrate has been injected into the reservoir from the injection well. Following injection of the final slug of concentrate, the injection water may be used as the aqueous drive fluid.

Alternatively, the slugs of aqueous displacement fluid may be formed by diluting
10 the concentrate into an injection water that is available at the injection site. In this case, it is preferred that the same injection water is used as for the aqueous spacer fluid such that the concentrate is intermittently dosed into the injection water. Suitably, injection of the injection water may be continued after the final dosing of the concentrate into the injection water such that the injection water serves as an aqueous drive fluid. Typically, the
15 injection water has a natural pH of less than 8.5, preferably, less than 8.0, for example, in the range of 6.0 to 8.0. Preferably, the initial concentration of zinc in each of the slugs of aqueous displacement fluid formed by diluting the concentrate into the injection water is maintained at above a concentration at which the natural pH of the slugs of aqueous displacement fluid is less than 5.5. Typically, the initial concentration of zinc in each of
20 the slugs formed by diluting the concentrate into the injection water is maintained at above a concentration of 0.8 mol/L, preferably, above a concentration of 1.0 mol/L, in particular, above a concentration of 1.5 mol/L.

Where the concentrate is diluted into the injection water, the amount of concentrate that is dosed into the injection water may be controlled using a metered pump to maintain
25 the concentration of zinc in each slug of aqueous displacement fluid at a near a target concentration, for example within $\pm 1\%$ of a target concentration. The amount of concentrate dosed into the injection water may be same or different for each slug. Further, the sizes of each of the slugs (formed by dosing concentrate into the injection water) may be the same or different, i.e., the concentrate may be dosed into the same or different
30 volumes of injection water. Similarly, the pore volumes of the aqueous spacer slugs may be the same or different, i.e., the same or different volumes of injection water may be injected after ceasing and before recommencing dosing of concentrate into the injection

water.

Where the natural pH of the concentrate delivered to the injection site is less than 3, in particular, less than 2, there may be a risk of corrosion of the tanks of a delivery tanker (for example, a tanker ship or tanker truck) or corrosion of any optional storage tank for the concentrate at the injection site.

Also, where the natural pH of the injected slugs of aqueous displacement fluid is less than 3, in particular, less than 2, there may be a risk of: (1) corrosion of manifolds, injection lines, injection tubing, well casings and liners and downhole equipment; and, (2) dissolving acid soluble material present in the reservoir such as carbonate cements.

The risk of corrosion of the tanks of a delivery tanker or of a storage tank located at the injection site may be mitigated when the tank is provided with a liner or coating formed from a corrosion resistant material such as titanium, fiberglass or a polymeric material (in particular, a rubber material). The corrosion risk for manifolds, injection lines, injection tubings, casings, liners and downhole equipment may be mitigated by constructing these items from a corrosion resistant steel, such as a steel alloy having a minimum 10.5% by weight chromium content.

However, it may be preferred to select a concentration of zinc halide that results in a natural pH for the concentrate of above 3, preferably, above 3.5 (provided that the pH is maintained at a value of below 5.5). Similarly, it may be preferred to select a concentration of zinc halide for the slugs of aqueous displacement fluid that results in a natural pH for the slugs of above 3, preferably above 3.5. Accordingly, it may be preferred that the concentrate or the slugs of aqueous displacement fluid have a concentration of zinc in the range of 0.85 to 2.75 mol/L, most preferably 0.1 to 2.75 mol/L.

However, it is also envisaged that a base may be added to concentrate at its production site (prior to the concentrate being transported to the injection site) or to the slugs of aqueous displacement fluid at the injection site to increase the pH of the concentrate or the slugs of aqueous displacement fluid to a value of at least 3, preferably, at least 3.5, most preferably, at least 4.0. Suitable bases include sodium hydroxide, potassium hydroxide, ammonium hydroxide, calcium hydroxide and magnesium hydroxide. Preferably, the amount of base added to the concentrate at its production site or to the slugs of aqueous displacement fluid at the injection site is controlled such that the pH is maintained at a value of less than 5.5, preferably less than 5.0. Owing to the cost of

transporting the base to the injection site, it is preferred that the base is added to the concentrate at its production site.

Given the risk of precipitation of insoluble zinc hydroxide at pH values of above 7.0, in particular, at values above 8.0, the method of the present invention is particularly
5 suitable for use in reservoirs, preferably, sandstone reservoirs, where the pH of the formation water is less than 7.0, preferably, less than 6.5, more preferably, in the range of 4.5 to 6.5. Typically, the pH is determined using a sample of formation water that has been removed from the reservoir, for example, using formation water that has been separated from a sample of produced fluids removed from a production well, or from a
10 flow line or using a sample of formation water that has been separated from oil and gas at a production facility. The person skilled in the art will understand that the pH is preferably determined immediately after the formation water is separated from the associated oil and gas phases.

In order to reduce the risk of precipitation of insoluble zinc hydroxide species, the
15 aqueous spacer fluid and any aqueous drive fluid suitably has a pH of less than 8.5 thereby mitigating the risk of the pH of the dispersively mixed fluids increasing to a value above 7.0. It is preferred that the aqueous spacer fluid and any aqueous drive fluid has a natural pH in the range of 6.5 to 8.5, preferably, 6.5 to 8.0, in particular, 6.5 to 7.5.

As disclosed in International Patent Application Publication No. WO 2015/007749,
20 the threshold concentration of zinc may be determined from coreflood experiments either under reduced conditions (at a laboratory temperature and pressure) or under reservoir conditions (at a temperature and pressure representative of reservoir conditions).

Typically, the coreflood experiments may be performed on a core plug taken from a core sample removed from the layer(s) of reservoir rock. The core plug is preferably reduced to
25 initial oil saturation using samples of the formation water and crude oil removed from the reservoir, and in the case of a reservoir condition coreflood test, the fluids are recombined with a gas having the same composition as the gas separated from the produced fluids at a production facility. However, a synthetic formation water may also be used, preferably, having the same composition as the formation water sampled from the reservoir.

30 Typically, a secondary coreflood test is performed in which an injection water is injected into the core sample until oil is no longer produced from the core sample followed by a tertiary coreflood test in which an aqueous displacement fluid comprising an aqueous

solution of the zinc halide salt in the injection water used in the secondary coreflood test is injected into the core sample. The threshold concentration, C_T , of zinc is the minimum concentration of zinc in the aqueous displacement fluid that is injected into the core sample at which incremental oil production is observed in the tertiary coreflood experiment. Such
5 coreflood tests are well known to the person skilled in the art. Alternatively, the threshold concentration of zinc may be determined using other well known methods in the art including single well chemical tracer (SWCT) tests, imbibition studies or from contact angle measurements.

The Reservoir Adsorption Capacity (RAC) for zinc may be determined from
10 coreflood experiments by analysis of the concentration of zinc in the aqueous phase of the effluent removed from the core sample (compared with a non-adsorbing tracer) or by static or dynamic adsorption measurements on a sample of reservoir rock (for example, a core sample).

The total pore volume, PVA , of the plurality of slugs of aqueous displacement fluid
15 that are injected into the layer(s) of reservoir rock is in the range of 10^{-8} to 10^{-1} , preferably, in the range of 10^{-7} to 10^{-2} , more preferably, in the range of 10^{-6} to 10^{-2} , most preferably, in the range of 10^{-5} to 10^{-3} of the swept pore volume (PVR).

The pore volume of each of the individual slugs of aqueous displacement fluid is in the range of 10^{-12} to 10^{-2} of the swept pore volume (PVR). Preferably, each individual slug
20 of aqueous displacement fluid has a pore volume in the range of 10^{-10} to 10^{-4} , more preferably, in the range of 10^{-9} to 10^{-4} of the PVR . It is to be understood that the pore volumes of each of the plurality of slugs of aqueous displacement fluid may be the same or different.

The person skilled in the art will understand that the number of slugs, n , of aqueous
25 displacement fluid will be dependent upon the total injected pore volume of the plurality of slugs of aqueous displacement fluid and the pore volume of each of the plurality of slugs of aqueous displacement fluid. Typically, there may be at least 15 slugs, preferably, at least 20 slugs of aqueous displacement fluid per pore volume swept by the injected fluids. Typically, there may be up to 1000 slugs, preferably, up to 500 slugs, more preferably up
30 to 100 slugs, for example, up to 50 slugs of aqueous displacement fluid per pore volume swept by the injected fluids. Suitably, there may be from 15 to 1000 slugs, preferably, 20 to 500 slugs, more preferably from 20 to 250 slugs, for example, from 20 to 100 slugs of

aqueous displacement fluid per pore volume swept by the injected fluids. In this context, the term “injected fluids” is taken to comprise the alternating slugs of aqueous displacement fluid and of aqueous spacer fluid and any subsequently injected aqueous drive fluid.

5 Suitably, the amount of zinc delivered to the layer(s) of reservoir rock by the plurality of slugs of aqueous displacement fluid is equal to or greater than the minimum quantity of zinc (MQ).

The total pore volume of the plurality of slugs of aqueous spacer fluid that are injected into the layer(s) of reservoir rock, is in the range of 0.9 to 0.9999999, preferably, 10 in the range of 0.99 to 0.9999999, more preferably, in the range of 0.99 to 0.999999, most preferably, in the range of 0.999 to 0.99999 (based on the swept pore volume).

Suitably, each individual slug of aqueous spacer fluid has a pore volume in the range of 0.0001 to 0.1000 (based on the swept pore volume). The pore volumes of the individual slugs of aqueous spacer fluid may be the same or different. Suitably, a slug of aqueous 15 spacer fluid may have a higher pore volume than an adjacent slug of aqueous displacement fluid (in the alternating sequence of slugs). For example, the ratio of the injected pore volume of an aqueous spacer slug to the injected pore volume of an adjacent slug of aqueous displacement fluid is preferably at least 2:1, most preferably, at least 3:1. Suitably, the ratio of the injected pore volume of a slug of aqueous spacer fluid to the 20 injected pore volume of an adjacent slug of aqueous displacement fluid is in the range of 2:1 to 1000:1, preferably, 3:1 to 500:1. The person skilled in the art will understand that the number of spacer slugs will be dependent upon the number of slugs of aqueous displacement fluid in the alternating sequence of slugs.

It is envisaged that the composition of the aqueous spacer fluid may be the same or 25 different for each spacer slug, preferably, the same. Typically, each individual slug of aqueous spacer fluid does not contain any added zinc salt or insubstantial amounts of added zinc salt. Suitably, each individual slug of aqueous spacer fluid has a concentration of zinc, $C_{Spacer-i}$, significantly below the threshold concentration, C_T , for zinc, for example, $C_{Spacer-i}$ may be less than 25%, preferably, less than 10%, more preferably, less than 5%, in 30 particular, less than 1% of the threshold concentration, C_T . Preferably, the aqueous spacer fluid has a zinc concentration of less than 0.001 mol/L, more preferably, less than 0.0001 mol/L, most preferably, less than 0.00001 mol/L.

As discussed above, an aqueous drive fluid may be injected into the layer(s) of reservoir rock from the injection well to sweep the dispersively mixed slugs (and hence the bank of released oil) through the layer(s) of reservoir rock towards a production well.

Typically, the aqueous drive fluid is injected into the layer(s) of reservoir rock in a pore volume of at least 1, preferably, at least 2, for example, in the range of 2 to 10. Typically, this aqueous drive fluid does not contain any added zinc salt or insubstantial amounts of added zinc salt. Suitably, the aqueous drive fluid contains an amount of zinc significantly below the threshold concentration, C_T , for zinc, for example, an amount that is less than 25%, preferably, less than 10%, more preferably, less than 5%, in particular, less than 1% of the threshold concentration. Preferably, the aqueous drive fluid has a zinc concentration of less than 0.001 moles/L, more preferably, less than 0.0001 moles/L³, most preferably, less than 0.00001 moles/L.

It is envisaged that a slug of aqueous spacer fluid may be injected into the layer(s) of reservoir rock before the first of the slugs of aqueous displacement fluid thereby minimizing mixing of the aqueous displacement fluid with the formation water. However, where the aqueous displacement fluid is compatible with the formation water, there is no requirement to inject a slug of aqueous spacer fluid before the first of the slugs of aqueous displacement fluid.

Similarly, a slug of aqueous spacer fluid may be injected into the layer(s) of reservoir rock after the final slug of aqueous displacement fluid and before injection of the aqueous drive fluid. However, where the aqueous drive fluid is compatible with the aqueous displacement fluid, there is no requirement for a spacer slug between the final slug of aqueous displacement fluid and the aqueous drive fluid.

By “compatible” is meant that mixing of the first slug of aqueous displacement fluid with the formation water (or of the last slug of aqueous displacement fluid with the aqueous drive fluid) does not result in precipitation of either insoluble mineral scales or insoluble zinc species arising from reaction of the zinc dissolved in the aqueous displacement fluid with any precipitating ion for the zinc that may be present in the formation water (or in the aqueous drive fluid).

The method of the present invention is intended for use in a sweet reservoir that produces negligible amounts of H₂S as injection of slugs of the aqueous displacement fluid into a sour reservoir may lead to precipitation of insoluble zinc sulfide within the reservoir

upon dispersive mixing of the aqueous displacement fluid (containing a dissolved zinc halide salt) with the formation water (containing dissolved hydrogen sulfide). A “sweet reservoir” is defined herein as a reservoir in which the formation water sampled from the reservoir has a concentration of dissolved sulphur of less than 2 mg/L, (0.0625 mmol/L),
5 more preferably, less than 1 mg/L (0.03125 mmol/L), yet more preferably, less than 0.5 mg/L (0.0156 mmol/L), in particular, less than 0.25 mg/L (0.0078 mmol/L). The person skilled in the art will understand that the concentration of sulfur (excluding sulfate) in the sampled formation water (which at a pH of less than 7.0 is typically in the form of hydrosulfuric acid) may be determined by analysis of a sample of formation water that is
10 separated from a sample of produced fluids taken at a wellhead, from a flow line or at a production facility. The formation water is analyzed, using techniques well known to the person skilled in art, for both total dissolved sulfur concentration (for example, by inductively coupled plasma atomic emission spectroscopy) and sulfate anion concentration (for example, by ion chromatography). The dissolved sulfur concentration, excluding
15 sulfate, is then determined by subtracting the sulfate anion concentration from the total dissolved sulfur concentration. The person skilled in the art will understand that the dissolved sulfur content of the formation water is determined immediately after separation of the formation water from the associated oil and gaseous phases. A “sweet reservoir” may also be defined as a reservoir in which the concentration of H₂S in the produced gas
20 phase that partitions from a pressurised sample of formation water (at a pH at or below 5) is less than 3 ppmv, preferably, less than 2 ppmv, more preferably, less than 1 ppmv, and is most preferably below the gas phase detection limit for H₂S of about 0.5 ppmv (measured at a Standard Temperature and Pressure (STP) of 0°C and 1 atmosphere absolute pressure).

The person skilled in the art would understand that when an aqueous displacement
25 fluid, aqueous spacer fluid or aqueous drive fluid contains levels of sulfate anions of greater than 40 ppmv, in particular, greater than 100 ppmv, there is a souring risk. This souring risk is increased when the aqueous displacement fluid, aqueous spacer fluid or aqueous drive fluid has levels of sulfate anions in the range of 0.5 to 5 mole%, in particular, 1 to 4 mole% (based on the total molar concentration of inorganic anions).

30 Souring of a reservoir is believed to arise from the production of hydrogen sulfide by sulfate-reducing bacteria (SRB) and may be mitigated by the presence of nitrate anions in the slugs of aqueous displacement fluid, in the slugs of aqueous spacer fluid or in the

aqueous drive fluid, as the nitrate anions stimulate nitrate-reducing, sulfide-oxidizing bacteria (NR-SOB) and heterotrophic nitrate-reducing bacteria (hNRB) that compete with SRB for biodegradable organic species. Generally, naturally occurring saline waters contain relatively low amounts of nitrate anions of less than 1 ppm, for example, less than 0.1 ppm. When the slugs of aqueous displacement fluid, the slugs of aqueous spacer fluid, or the aqueous drive fluid have a concentration of sulfate that presents a souring risk for the reservoir, one or more nitrate salts may be added to one or more of these fluids. Typically, the nitrate salt(s) is added to the slugs of aqueous displacement fluid, the slugs of aqueous spacer fluid or the aqueous drive fluid in an amount that gives a nitrate anion concentration of at least 5 ppmv (0.08 mmol/L), preferably at least 10 ppmv (0.16 mmol/L). Preferably, the nitrate salt(s) is added to the slugs of aqueous displacement fluid, the slugs of aqueous spacer fluid or the aqueous drive fluid in an amount that gives a nitrate anion concentration in the range of 10 to 500 ppmv (0.16 to 8 mmol/L, more preferably, in the range of 10 to 100 ppmv (0.16 to 1.6 mmol/L).

However, the risk of souring of the reservoir may also be mitigated when:

1. The plurality of slugs of aqueous displacement fluid are injected into the reservoir as an undiluted concentrate wherein the concentrate has a concentration of sulfate anions of less than 40 ppmv.
2. The slugs of aqueous displacement fluid are formed by diluting the concentrate having a concentration of sulfate anions of less than 40 ppmv into an injection water selected from a naturally occurring low salinity water such as river water, lake water, low salinity aquifer water, low salinity produced water (low salinity water separated from oil at a production facility) wherein the naturally occurring low salinity water has a concentration of sulfate anions of less than 40 ppmv.
3. The slugs of aqueous displacement fluid are formed by diluting the concentrate having a sulfate anion concentration of less than 40 ppmv into a sulfate reduced injection water formed by removing sulfate anions from a naturally occurring saline water such as seawater, estuarine water, produced water (saline produced water separated from oil at a production facility) or saline aquifer water wherein the sulfate reduced injection water has a sulfate concentration of less than 40 ppmv.
4. The slugs of aqueous displacement fluid are formed by diluting the concentrate having a sulfate anion concentration of less than 40 ppmv into a desalinated injection water

having a sulfate anion concentration of less than 40 ppmv, preferably, less than 25 ppmv.

The risk of souring of the reservoir may also be mitigated when the aqueous spacer fluid or aqueous drive fluid is selected from:

1. Naturally occurring low salinity injection waters (as defined above) having a sulfate concentration of less than 40 ppmv;
2. Sulfate reduced injection waters (as defined above) having a sulfate concentration of less than 40 ppmv; or
3. Desalinated injection waters (as defined above) have a sulfate concentration of less than 40 ppmv.

A sulfate reduced injection water may be produced by contacting a naturally occurring saline water (feed water) having a relatively high sulfate concentration, for example, seawater, estuarine water, or brackish water, with a nanofiltration membrane that selectively excludes sulfate anions whilst allowing monovalent ions such as Group IA metal ions (e.g. sodium ions) and halide ions (e.g. chloride ions and bromide ions) to pass therethrough thereby producing a permeate (hereinafter “NF permeate”) comprising a sulfate reduced saline water having a lower concentration of sulfate anions and a retentate having a higher concentration of sulfate anions than the feed water. Thus, the NF permeate (sulfate reduced saline water) removed from a nanofiltration membrane typically has a sulfate concentration of less than 40 ppmv, preferably, less than 25 ppmv.

It is also envisaged that a sulfate reduced injection water may be formed by adding precipitating counter-cations, such as barium or strontium cations, to a naturally occurring saline water that contains high levels of sulfate anions thereby forming insoluble sulfate salts of the precipitating cation, such as barium sulfate or strontium sulfate, which may then be separated from the saline water by filtration or centrifugation.

A desalinated injection water may be formed by treating a naturally occurring saline water using reverse osmosis (RO) to generate a treated water (i.e., a permeate that passes through the RO membrane) that is substantially free of sulfate anions and of other dissolved solids. Typically, the permeate that passes through an RO membrane (hereinafter “RO permeate”) has a total dissolved solids content of less than 500 ppmv, for example, less than 200 ppmv, and a sulfate anion concentration below 40 ppm, preferably below 25 ppmv. However, in order to mitigate the risk of formation damage arising from swelling and migration of clays, the RO permeate may be mixed with NF permeate to

increase the total dissolved solids content of the desalinated injection water, typically, to a value in the range of 1000 to 5000 ppmv, preferably, to a value in the range of 2000 to 3000 ppmv.

The use of sulfate reduced injection waters or desalinated injection waters also has the advantage of mitigating the risk of forming insoluble mineral scales comprised of water-insoluble sulfate salts.

Modelling studies have shown that injection of alternating slugs of aqueous displacement fluid and aqueous spacer fluid into at least one layer of reservoir rock having a dimensionless dispersivity in the range of 1 to 30%, has the effect of exposing the portion of the layer(s) of the reservoir close to the injection well, in particular, the first 5% of the swept pore volume of layers(s) of the reservoir, to a higher zinc concentration (compared with continuous injection of the aqueous displacement fluid when: (i) the same total amount (weight or molar amount) of zinc is injected into the layer(s) of reservoir rock; and (ii) the pore volume of the continuously injected aqueous displacement fluid ($PV_{\text{continuous injection}}$) is the same as the total pore volume of the alternating slugs of aqueous displacement fluid and of the aqueous spacer fluid ($PV_{\text{total of alternating slugs}}$). This may be advantageous in releasing additional incremental oil from the portion of the layer(s) of reservoir rock closest to the injection well.

Modelling studies have also shown that injection of alternating slugs of aqueous displacement fluid and aqueous spacer fluid into at least one layer of reservoir rock having a dimensionless dispersivity in the range of 1 to 30%, has the effect of providing a similar profile for the maximum zinc concentration in the dispersively mixed slugs of aqueous displacement fluid and of aqueous spacer fluid compared with continuous injection of the aqueous displacement fluid when : (i) the same total amount (weight or molar amount) of zinc is injected into the layer(s) of reservoir rock; and, (ii) the pore volume of the continuously injected aqueous displacement fluid ($PV_{\text{continuous injection}}$) is the same as the total pore volume of the alternating slugs of aqueous displacement fluid and of aqueous spacer fluid ($PV_{\text{total of alternating slugs}}$).

An advantage of injecting a plurality of slugs of aqueous displacement fluid separated by aqueous spacer slugs is that there is no requirement to have a storage tank for the aqueous displacement fluid at the injection site. Instead, as discussed above, a concentrate comprising a concentrated aqueous solution of a zinc halide selected from zinc

chloride, zinc bromide and mixtures thereof may be transported by tanker to the injection site of the reservoir. This concentrate may be injected directly from the tanker into the injection system for the injection well(s) (either with or without dilution into an injection water). This is particularly advantageous for an offshore reservoir as there may be space and weight limitations for an offshore platform or Floating Production and Offloading Facility (FPSO).

In an embodiment of the method of the present invention, the aqueous displacement fluid, in the form of a concentrate, may be transported to the injection site of an offshore reservoir by a tanker ship and may be injected directly into the injection system for either a single injection well or for a plurality of injection wells, from the tanker ship. Suitably, the aqueous displacement fluid is injected into a subsea injection system for the injection well(s) from the tanker ship. The offloading tanker ship may be moored to a single-point mooring (SPM), *i.e.*, a loading buoy anchored offshore, that serves both as a mooring point and as an interconnect for the tanker ship. Thus, the SPM is in fluid communication with both the injection system for the injection well(s) and the offloading tanker ship.

Typically, the loading buoy is provided with mooring and anchoring elements, a rotating part, a swivel and a fluid transfer system. The swivel is the connection between geostatic and rotating parts of the loading buoy and enables the offloading tanker ship to rotate (weathervane) with respect to the loading buoy when the tanker ship is moored to the buoy.

Typically, the tanker ship is moored to the loading buoy by means of a hawser arrangement. Typically, the fluid transfer system of the loading buoy comprises a riser connected between the loading buoy and the subsea injection system and a floating hose string connected between the loading buoy and the offloading tanker ship. However, it is also envisaged that the method of the present invention may be used with an onshore reservoir where the concentrate is delivered to the injection site by tanker trucks.

Typically, the volumetric slug size of each of the individual slugs of aqueous displacement fluid is limited by the volumetric delivery capacity of the tanker (tanker ship or tanker truck) that delivers the concentrate to the injection site. The volumetric slug size is limited by the tanker delivery volume (L) and a dilution factor wherein the dilution factor is the volumetric fraction of concentrate in the slug of aqueous displacement fluid. For avoidance of doubt, the tanker delivery volume is the volume of concentrate contained in the tanker prior to off-loading. Typically, the dilution factor is in the range of 0.1 to 1

(10 to 100% by volume of concentrate in the injected slug of aqueous displacement fluid), preferably, 0.2 to 1 (20 to 100% by volume of concentrate in the injected slug of aqueous displacement fluid). Thus, when the concentrate is injected into the injection well(s) without dilution into an injection water, the dilution factor is 1. The dilution factor will be dependent upon the concentration of zinc in the concentrate (in weight/L or moles/L) and the target concentration of zinc in the slugs of aqueous displacement fluid (in weight/L or moles/L) that are to be injected into the layer(s) of reservoir rock. Where the injection system is in fluid communication with a plurality of injection wells, the slug size for each individual injection well is also dependent upon the weight fraction (or mole fraction) of zinc to be injected into the layer(s) of reservoir rock from each individual injection well.

The volumetric slug size for a single well may be determined as follows:

volumetric slug size = tanker delivery volume $\times$ dilution factor.

The volumetric slug size for an individual injection well of a plurality of injection wells may be determined as follows:

volumetric slug size = tanker delivery volume $\times$ dilution factor $\times$ weight fraction (or mole fraction) of zinc injected into the individual injection well.

Where, equal weight fractions (or mole fractions) of zinc are injected into a plurality of injection wells, n , the weight fraction (or mole fraction) is taken to be $1/n$. However, it is also envisaged that different weight fractions (or mole fractions) of zinc may be injected into each of the plurality of injection wells.

It is envisaged that, where the concentrate is diluted into an injection water, the initial concentration of zinc (and hence the initial weight or initial moles of zinc) in each of the plurality of slugs of aqueous displacement fluid may be the same or different.

Different initial concentrations of zinc halide salt may be achieved in the slugs by adjusting the dilution factor for the concentrate. Losses of zinc to the reservoir (for example, through adsorption on the reservoir rock) may be higher at the front of the dispersively mixed fluids. Accordingly, the initial concentration of zinc may decrease with each successively injected slug of aqueous displacement fluid in order to take into account losses of zinc to the reservoir. Without wishing to be bound by any theory, it is believed that at least a portion of the adsorbed zinc may desorb from the reservoir rock into the aqueous spacer slugs over the travel distance at which at least a portion of each spacer slug remains intact in the reservoir. It is also believed that at least a portion of the adsorbed

zinc may desorb from the reservoir rock into any subsequently injected aqueous drive fluid.

The initial concentration of zinc in the slugs of aqueous displacement fluid may be selected such that at least a portion of the dispersively mixed fluids has a zinc

5 concentration that remains above a target zinc concentration at a set (or fixed) travel distance through the layer(s) of reservoir rock from the injection well. Suitably, the target concentration of zinc at the set travel distance is at least the threshold concentration, C_T , for zinc at which incremental oil recovery is detectable with aqueous solutions of zinc halide salts in coreflood experiments (hereinafter “target concentration”). Preferably, the target
10 concentration is at least two times C_T , more preferably, at least 5 times C_T . Preferably, the target concentration of zinc may be at least 0.0050 mol/dm^3 , preferably, at least 0.0075 mol/dm^3 at the set (or fixed) travel distance. Suitably, the set travel distance through the layer(s) of reservoir rock may be at least 25%, preferably, at least 50% of the interwell distance between the injection well and production well.

15 Modelling studies using a transportation mixing module of a geochemical model may be used to determine the optimal initial concentration of zinc for different sized pore volume slugs of aqueous displacement fluid that achieves the desired target zinc concentration in the dispersively mixed fluids at the set travel distance.

Typically, the target zinc concentration in the dispersively mixed fluids at the set
20 travel distance is dependent upon the initial concentration of zinc in each of the plurality of slugs of aqueous displacement fluid, the pore volumes of each of the slugs of aqueous displacement fluid, the pore volumes of each of the spacer slugs, losses of zinc to the reservoir and the reservoir dispersivity as a percentage or fraction of the set travel distance through the layer(s) of reservoir rock. The person skilled in the art will understand that as
25 each slug of aqueous displacement fluid begins to dispersively mix with adjacent slugs of aqueous spacer fluid, the concentration profiles will evolve over time. For example, initially, the concentration profile for each individual dispersively mixing slug of aqueous displacement fluid may have a normal distribution such that the concentration is at a maximum in the middle of each slug and tapers symmetrically at the front and rear of the
30 slugs or an asymmetric distribution such that the maximum concentration is skewed (i.e. is offset from the middle of the slug). An asymmetric concentration distribution may occur where the reservoir is heterogeneous i.e., there is a variation in physical properties of the

reservoir rock (for example, porosity or permeability) with location within the reservoir. It is envisaged that, eventually, each of the slugs of aqueous displacement fluid may become completely mixed with the adjacent spacer slugs such that the slugs merge within the layer(s) of reservoir rock to form a single diluted slug of aqueous displacement fluid. If
5 so, the target concentration refers to the concentration of the merged diluted slug at the selected travel distance.

Without wishing to be bound by any theory, it is believed that the zinc in the dispersing slugs of aqueous displacement fluid releases additional components of the crude oil that would not otherwise be released from the pores of the reservoir rock by
10 waterflooding the reservoir with the water used as the aqueous solvent for the aqueous displacement fluid or the water used as the aqueous spacer fluid (i.e. a water that does not contain a zinc halide salt additive). Accordingly, a “bank of released oil” is swept through the reservoir towards the production well. Thus, an advantage of the method of the present invention is that the dispersing slugs of aqueous displacement fluid and of aqueous spacer
15 fluid provide a similar concentration profile for zinc within the layer(s) of reservoir rock compared with continuous injection of the aqueous displacement fluid (when the same quantity of zinc is injected into the layer(s) of reservoir rock in slugging mode as in continuous injection mode and the total pore volume of the alternating slugs of aqueous displacement fluid and of aqueous spacer fluid is substantially the same as the pore volume
20 of the continuously injected aqueous displacement fluid).

The alternating slugs of aqueous displacement fluid and of aqueous spacer fluid are preferably injected, under pressure, into at least one injection well that is spaced from a production well such that the aqueous displacement fluid passes into the at least one layer of reservoir rock. The passage of the dispersing slugs through the layer(s) of the reservoir
25 rock displaces oil from the rock surface and forces the displaced oil ahead of it, and towards the production well from which the oil is recovered. Preferably, the injection well and production well are spaced apart in a lateral direction i.e. are not overlying.

The swept pore volume (defined above) between an injection well and the associated production well(s) may be readily determined by methods known to the person skilled in
30 the art. Thus, the swept pore volume may be determined by passing a high salinity water having an inert tracer contained therein through the layer(s) of reservoir rock from the injection well to the production well(s). The swept pore volume may also be determined

using modeling studies. These modeling studies employ a reservoir simulator into which has been imported a static geological model of the reservoir. This static geological model is obtained by inputting seismic imaging data and petrophysical data (such as the porosity and permeability of the layer(s) of reservoir rock, mineralogical data, the initial water saturation of the reservoir, and the initial oil saturation of the reservoir) thereby generating a 3 dimensional (3-D) model of the reservoir showing the layers of the reservoir rock, traps and any faults and incorporating petrophysical data associated with one or more layers of the reservoir. The locations of the injection well(s) and production well(s) are subsequently inputted into the reservoir simulator together with additional fluid properties such as the relative permeabilities of the reservoir rock to oil and water. The reservoir simulator is then used to model injection of fluids into the one or more layers of reservoir rock via the injection well(s), movement of fluids through one or more layers of the reservoir, in particular, the oil-bearing layers, and production of fluids from the reservoir via the production well(s). The reservoir simulator model may also be updated using 4-dimensional (4-D) seismic imaging data i.e. seismic imaging data obtained at one or more points in time following commencement of oil production from the reservoir. The reservoir simulator may be used to determine the swept pore volume between an injection well and one or more production wells by modeling the movement of an injected fluid comprising a tracer from the injection well to the production well(s). The swept pore volume differs from a pore volume determined using the volume of the oil-bearing layer(s) between the injection well and production well(s) and the porosity of the reservoir rock as the swept pore volume takes into account barriers to flow such as a reduction in permeability of the layer(s) of reservoir rock.

As discussed above, there may be one injection well and one production well, but preferably there may be more than one injection well and more than one production well. The person skilled in the art will understand that depending on the spatial arrangement of the injection well and its associated production wells, the aqueous displacement fluid may break-through into each production well at different times.

The method of the invention may be used at commencement of oil production from the reservoir (omitting primary recovery), in secondary recovery mode (after primary recovery of oil under the natural pressure of the reservoir) or in tertiary recovery mode (for example, after a waterflood with a water that does not contain any zinc halide salt

additive).

The person skilled in the art will understand that in secondary recovery mode, fluid is injected into the formation from an injection well in order to maintain the pressure in the formation and to sweep oil towards a production well. An advantage of injecting the alternating slugs of aqueous displacement fluid and of aqueous spacer fluid into the layer(s) of reservoir rock during secondary recovery is that the zinc releases additional oil from the pores of the reservoir rock. Accordingly, there may be a longer period of dry oil recovery from the production well thereby deferring water break-through. In addition, even after water break-through, there may be enhanced recovery of oil compared with using the injection water used as the aqueous spacer fluid and potentially less water production. Also, there may be less water production (a higher oil to water ratio) for a given volume of produced fluid compared with using the injection water employed as the aqueous spacer fluid. These advantages also apply if the method of the present invention is used at commencement of oil production from a reservoir.

The person skilled in the art will understand that in tertiary recovery, injection of the original fluid is stopped and a different fluid is injected into the layer(s) of reservoir rock for enhanced oil recovery. Thus, the fluids injected into the layer(s) of reservoir rock during tertiary recovery are the alternating slugs of the aqueous displacement fluid and the aqueous spacer fluid, and the fluid that has previously been injected into the layer(s) of reservoir rock during secondary recovery may be a water that does not contain an added zinc halide salt). Typically, the previously injected water may be seawater, estuarine water, brackish water, produced water, aquifer water, river water, lake water, desalinated water or a mixture thereof.

The present invention will now be illustrated by reference to the following Examples and Figures.

Example 1 – pH Experiments

Solutions of zinc halide salts were prepared in deionised water (DI), low salinity water (LSW) and synthetic seawater (SW) across a range of zinc concentrations. The pH of each of the solutions was then measured. The composition of the LSSW and SW are given in Table 1 below and the pH data for the various zinc halide solutions are presented in Tables 2 to 4 below.

Table 1

Salt	LSW (mg/L)	SW (mg/L)
NaHCO ₃	191.37	6.28
CaCl ₂	1107.82	36.43
MgCl ₂	4987.85	163.60
KCl	724.57	23.77
NaCl	23478.11	770.08
TDS (mg/L)	30490	1000

Table 2 – pH measurements for zinc chloride solutions

5

[ZnCl ₂] (mol/L)	pH DI Water	pH LSW	pH SW
5.458	1.924	1.813	1.490
3.978	2.853	2.788	2.610
2.740	3.580	3.555	3.430
1.688	4.243	4.222	4.130
0.844	5.080	5.082	4.923
0.0149	7.104	6.912	6.457
0.0074	7.328	7.096	6.655

It can be seen that at concentrations of zinc chloride of at least 0.844 moles/L that the pH values of the solutions of zinc chloride in deionized water, low salinity water and seawater are about 5. Further, it can be seen that a concentration of zinc chloride of 2.740 mol/L, the pH of the zinc chloride solution in deionized water, low salinity water and seawater is about 3.5.

10

Table 3 – pH measurements for zinc bromide solutions

[ZnBr ₂] (mol/L)	pH DI water	pH LSSW	pH SW
5.458	0.709	0.809	0.912
3.978	1.27	1.266	1.56
2.74	1.768	1.797	2.24
1.688	2.391	2.468	3.002
0.844	3.609	3.709	4.286
0.0149	5.326	6.118	6.482
0.0074	5.515	6.545	6.26

It can be seen that at concentrations of at least 0.844 moles/L of zinc, the pH values of the solutions of zinc bromide in deionized water, low salinity water and seawater are about 4.

Table 4 – pH measurements for zinc iodide solutions

[ZnI₂] (moles/L)	pH DI Water	pH LSSW	pH SW
5.458	2.566	2.493	2.454
3.978	3.13	3.028	2.958
2.74	3.663	3.554	3.508
1.688	4.389	4.33	4.125
0.844	5.195 ^a	5.184 ^a	5.115 ^a
0.0149	6.235	6.494	6.517
0.0074	6.48	6.782	6.728

a. Precipitates observed.

The observation of precipitates for solutions of zinc iodide having a concentration of 0.844 moles/L may preclude the use of zinc iodide as an additive for an aqueous displacement fluid. Thus, there is a risk of zinc iodide precipitates forming under reservoir conditions because formation waters often have pH values of about 5.

Example 2 - Transportation Mixing Modelling

A transportation mixing module of a geochemical model was used to model mixing of the alternating slugs of aqueous displacement fluid and of aqueous spacer slugs. The transportation mixing module was a single phase one dimensional transportation mixing module. The one dimensional transportation mixing module comprised a plurality of cells arranged in series through which fluids were shifted (displaced). The total number of cells in the series was taken to contain one pore volume of fluid. Accordingly, a fraction of the cells was taken to contain a fractional pore volume of fluid. When modelling injection of alternating slugs of aqueous displacement fluid and of aqueous spacer fluid, each of the cells of the series initially contained formation water and, for each shift, either aqueous displacement fluid or aqueous spacer fluid was introduced to the first cell in the series, fluids contained in the first and successive cells were shifted (displaced) to the next cell in the series, and fluids removed from the last cell in the series were disregarded. Thus, if

there were n cells, introduction of one pore volume of fluids into the cells required n shifts. Typically, the number of cells, n , in the transportation mixing module was at least 10, preferably, 20 to 2000, for example, 50 to 1500. Mixing between the fluids contained in the cells was introduced as the fluids advanced through each cell of the series with the amount of mixing in each cell being determined from an inputted dispersivity value in the range of 1 to 30%, preferably, 2 to 25%, in particular, 2 to 10% (wherein the dispersivity was defined as a percentage of the number of cells of the transportation mixing module). Thus, mixing increased with both increasing dispersivity and with increasing number of shifts. The person skilled in the art will understand that as the fluids were shifted, the slugs of aqueous displacement fluid and the slugs of aqueous spacer fluid may become completely mixed in one of the cells of the series and consequently mixing of fluids may extend to other cells in the series. After the desired total fractional pore volume of aqueous displacement fluid was introduced to the series of cells, thereafter, for each shift, an aqueous drive fluid was introduced into the first cell in the series until the aqueous drive fluid had been shifted (displaced) through each of the cells in the series.

Modelling Results

A one dimensional reservoir mixing model (PHREEQC model) having 1000 cells (1000 L total pore volume) was used to simulate transportation of zinc chloride through a reservoir in two different modes:

- (1) Continuous injection of an aqueous displacement fluid consisting of an aqueous solution of zinc chloride into the cells; and
- (2) Alternating injection of slugs of an aqueous solution of zinc chloride and aqueous spacer slugs into the cells.

Simulations were performed under the conditions of Table 1 with either continuous injection of 1.0 pore volumes of an aqueous solution of zinc chloride or with injection of a total of 1.0 pore volumes of alternating slugs of aqueous displacement fluid and of aqueous spacer solution (each slug may occupy more than one cell). Simulations were also performed under the conditions of Table 2 with either continuous injection of 0.2 pore volumes of an aqueous solution of zinc chloride followed by injection of 0.8 pore volumes of an aqueous drive fluid or with injection of a total of 0.2 pore volumes of alternating slugs of an aqueous solution of zinc chloride and aqueous spacer solution followed by 0.8 pore volumes of an aqueous drive fluid. Thus, for each simulation, a total of one pore

volume of fluid(s) was introduced into the cells. The same total quantity of zinc chloride (100 moles) and the same reservoir dispersivity of 1% was used in all simulations. Simulations were performed both with and without selecting a value for reservoir adsorption capacity in the model.

5

Table 1: PHREEQC simulations using one pore volume of continuously injected aqueous displacement fluid or one pore volume of alternating slugs of aqueous displacement fluid and of aqueous spacer fluid

Simulation	Number of Slugs of Aqueous Displacement Fluid	Ratio of Aqueous Spacer Slugs to Slugs of Aqueous Displacement Fluid	Dispersivity (%)	Reservoir Adsorption Capacity (mol/PV)
1	Continuous Injection (1000)	Not applicable	1.0	0
2	20	1:1	1.0	0
3	50	3:1	1.0	0
4	Continuous Injection (1000)	Not applicable	1.0	25
5	20	1:1	1.0	25
6	50	3:1	1.0	25

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Table 2: PHREEQC simulations – 0.2 pore volumes of continuously injected aqueous displacement fluid or of alternating slugs of aqueous displacement fluid and of aqueous spacer fluid

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Simulation	Number of Slugs of Aqueous Displacement Fluid	Ratio of Aqueous Spacer Slugs to Slugs of Aqueous Displacement Fluid	Dispersivity (%)	Reservoir Adsorption Capacity (mol/PV)
7	Continuous Injection (200)	0	1.0	0
8	50	3:1	1.0	0
9	Continuous Injection (200)	0	1.0	25
10	50	3:1	1.0	25

The profiles for the maximum zinc concentrations in the dispersively mixing slugs recorded along the reservoir after injection of 0.25 pore volumes of fluids for simulations performed under the conditions of Table 1 are shown in Figures 1a and 1b. Similarly, the profiles for the maximum zinc concentrations after injection of 0.25 pore volumes of fluids for simulations performed under the conditions of Table 2 are shown in Figures 2a and 2b. Figures 1a and 2a are profiles obtained with adsorption of zinc switched off in the model while Figures 1b and 2b are profiles obtained with adsorption of zinc switched on in the model. Figures 1a and 1b show the profiles for simulations with continuous injection of an aqueous solution of zinc chloride and the profiles for simulations with injection of 20 and 50 slugs of aqueous solution of zinc chloride separated by aqueous spacer slugs. Figures 2a and 2b show the profiles for simulations with continuous injection of an aqueous solution of zinc chloride and for simulations with injection of 50 slugs of aqueous solution of zinc chloride separated by aqueous spacer slugs. As the same weight of zinc chloride was injected into the transportation mixing module for all simulations, the modelling of injection of alternating slugs necessitated an increase in the concentration of zinc chloride in the slugs of aqueous displacement fluid compared with modelling of continuous

injection of the aqueous solution of zinc chloride. It can be seen that the simulations in which there is adsorption of zinc sharpens the front of zinc in the model. Surprisingly, it was found that after injection of 0.25 pore volumes of fluids, the zinc concentration profiles for continuous injection of aqueous displacement fluid are similar to those for
5 injection of alternating slugs of aqueous displacement fluid and of aqueous spacer fluid. However, there is a higher concentration of zinc in the dispersively mixing slugs in the initial portion of the reservoir (initial 0.05 PV of the reservoir) compared with the simulations employing continuous injection of the aqueous displacement fluid.

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Claims:

1. A method for recovering crude oil from a reservoir comprising at least one layer of reservoir rock having crude oil and a formation water within the pore space thereof wherein the layer(s) of reservoir rock is penetrated by at least one injection well and at least one production well, the method comprising:

injecting into the layer(s) of reservoir rock from the injection well, alternating slugs of an aqueous displacement fluid comprising an aqueous solution of a zinc halide salt selected from zinc chloride, zinc bromide and mixtures thereof and of an aqueous spacer fluid characterized in that:

- (a) the pH of each of the slugs of aqueous displacement fluid is less than 5.5 and the pH of each of the slugs of aqueous spacer fluid is less than 8.5;
- (b) the number of injected slugs of aqueous displacement fluid, n , is in the range of 15 to 1000 per swept pore volume, PVR , of the layer(s) of reservoir rock;
- (c) the injected pore volume of each individual slug, PV_{Slug-i} , of aqueous displacement fluid is in the range of 10^{-12} to 10^{-2} of the swept pore volume, PVR , of the layer(s) of reservoir rock:

$$10^{-12} \leq PV_{Slug-t} \leq 10^{-2};$$

- (d) the total injected pore volume of the slugs of aqueous displacement fluid is in the range of 10^{-8} to 10^{-1} of the swept pore volume, PVR , of the layer(s) of reservoir rock:

$$10^{-8} \leq \sum_{t=1}^n PV_{Slug-t} \leq 10^{-1};$$

- (e) the injected pore volume of each individual slug of aqueous spacer fluid, $PV_{Spacer-i}$, is in the range of 0.0001 to 0.1000 of the swept pore volume, PVR , of the layer(s) of reservoir rock:

$$0.0001 \leq PV_{Spacer-t} \leq 0.1000;$$

- (f) the total injected pore volume of the slugs of aqueous spacer fluid is in the range of 0.9000000 to 0.9999999 of the swept pore volume, PVR , of the layer(s) of reservoir rock;

$$0.9000000 \leq \sum_{t=1}^n PV_{Spacer-t} \leq 0.9999999;$$

- (g) the reservoir rock has a dispersivity, α , in the range of 1 to 30% of the interwell distance between the injection well and production well; and

(h) the quantity of zinc delivered to the layer(s) of reservoir rock by the plurality of slugs of aqueous displacement fluid is equal to or greater than a predetermined minimum quantity (MQ).

2. A method as claimed in claim 1 wherein the minimum quantity of zinc, MQ , delivered to the layer(s) of reservoir rock by injecting the plurality of slugs of aqueous displacement fluid is determined using Equation 1 below:

$$MQ = \left[C_{InjAvg} \cdot (4\sqrt{\alpha} \operatorname{erf}^{-1} \left\{ \frac{c_T}{C_{InjAvg}} \right\}) + RAC \right] \cdot PVR \quad (1)$$

wherein RAC is the adsorption capacity of the reservoir, C_T is the threshold concentration for zinc, C_{InjAvg} is the initial average concentration of zinc for the alternating slugs of

10 aqueous displacement fluid and of aqueous spacer fluid, α is the dispersivity of the reservoir rock and PVR is the swept pore volume of the layer(s) of reservoir rock.

3. A method as claimed in claim 2 wherein C_{InjAvg} is determined using Equation 2 below:

$$C_{InjAvg} = \frac{\sum_{i=1}^n (C_{Slug-i} \cdot PV_{Slug-i})}{\sum_{i=1}^n (PV_{Slug-i} + PV_{Spacer-i})} \quad (2)$$

15 wherein C_{Slug-i} is an initial concentration of zinc in an individual slug of aqueous displacement fluid.

4. A method as claimed in any one of the preceding claims wherein an aqueous drive fluid is injected into the layer(s) of reservoir after injecting the alternating slugs of aqueous displacement fluid and of aqueous spacer fluid and the aqueous drive fluid has a pH of less
20 than 8.5.

5. A method as claimed in any one of the preceding claims wherein the ratio of the injected pore volume of an individual slug of aqueous spacer fluid to the injected pore volume of an adjacent slug of aqueous displacement fluid in the range of 2:1 to 1000:1, preferably, 3:1 to 500:1.

25 6. A method as claimed in any one of the preceding claims wherein the aqueous displacement fluid is intermittently delivered to an injection site of the reservoir by a tanker in the form of an concentrate comprising a solution of zinc chloride in an aqueous solvent selected from fresh water, potable water, distilled water and deionized water wherein the concentrate has (i) a natural pH of 5.5 or less and (ii) a concentration of zinc
30 chloride of at least 10% by weight, preferably, at least 15% by weight, most preferably, at least 20% by weight and of less than the saturation concentration of zinc chloride at the

ambient conditions at the injection site, and wherein the concentrate is injected directly from the tanker into an injection system for the injection well(s).

7. A method as claimed in claim 6 wherein the concentrate contains from 0 to 10 mole%, more preferably, from 0 to 5 mole%, in particular, from 0 to 2 mole% of zinc bromide based on the total molar amount of zinc chloride and of any zinc bromide in the concentrate.

8. A method as claimed in claims 6 or 7 wherein the concentrate has a natural pH of less than 3 and a base is added to the concentrate prior to its delivery to the injection site to adjust the pH of the concentrate to a value in the range of 3 to 5.5, preferably, 3.5 to 4.5.

9. A method as claimed in any one of claims 6 to 8 wherein the tanker is a tanker ship and is moored to a loading buoy at the injection site wherein the loading buoy serves both as a mooring point and as an interconnect between the tanker ship and the injection system for the injection well(s) and the aqueous displacement fluid is injected directly from the tanker ship into the injection system for the injection well(s) via the loading buoy.

10. A method as claimed in any one of claims 6 to 9 wherein prior to the tanker arriving at the injection site, an injection water is injected into the injection system for the injection well and when the tanker arrives at the injection site either:

(a) injection of the injection water into the injection system is interrupted and the concentrate is delivered from the tanker to the injection system for the injection well(s)

such that the concentrate serves as a slug(s) of aqueous displacement fluid and, after the tanker has finished delivering the concentrate to the injection system, injection of the injection water into the injection system recommences such that the injection water serves as a slug(s) of aqueous spacer fluid; or

(b) injection of the injection water into the injection system is continued and the concentrate is delivered from the tanker to a mixing point of the injection system where the concentrate is diluted into the injection water such that the diluted concentrate serves as a slug(s) of aqueous displacement fluid and, after the tanker has finished delivering the concentrate to the mixing point, injection of the injection water is continued such that the injection water serves as a slug(s) of aqueous spacer fluid.

11. A method as claimed in claim 10 wherein the tanker either:

(a) delivers a slug of aqueous displacement fluid to a single injection well and the volumetric size of the slug is determined as follows:

volumetric slug size = tanker delivery volume x volumetric dilution factor; or
(b) delivers a slug of aqueous displacement fluid to each of a plurality of injection wells
and the volumetric size of a slug delivered to an individual injection well of the plurality of
injection wells is determined as follows:

5 volumetric slug size = tanker delivery volume x volumetric dilution factor x
fraction of zinc injected into the layer(s) of reservoir rock from the individual injection
well.

12. A method as claimed in any one of claims 10 to 11 wherein the injection water is a
sulfate reduced injection water having a sulfate anion concentration of less than 40 ppmv.

10 13. A method as claimed in claim 12 wherein the sulfate reduced injection water is a
saline water having a total dissolved solids content of at least 17,500 ppmv, preferably, at
least 30,000 ppmv.

14. A method as claimed in any one of the preceding claims wherein from 15 to 1000
slugs, preferably, 20 to 500 slugs, more preferably, 20 to 250 slugs, in particular, from 20
15 to 100 slugs of aqueous displacement fluid are injected into the layer(s) of reservoir rock
per swept pore volume.

15. A method as claimed in any one of the preceding claims wherein the reservoir is a
sandstone reservoir having a formation water with a pH in the range of 4.5 to 6.5.

16. A method as claimed in any one of Claims 10 to 15 wherein the injection water has a
20 pH in the range of 6.5 to 8.5, preferably, 6.5 to 7.5.

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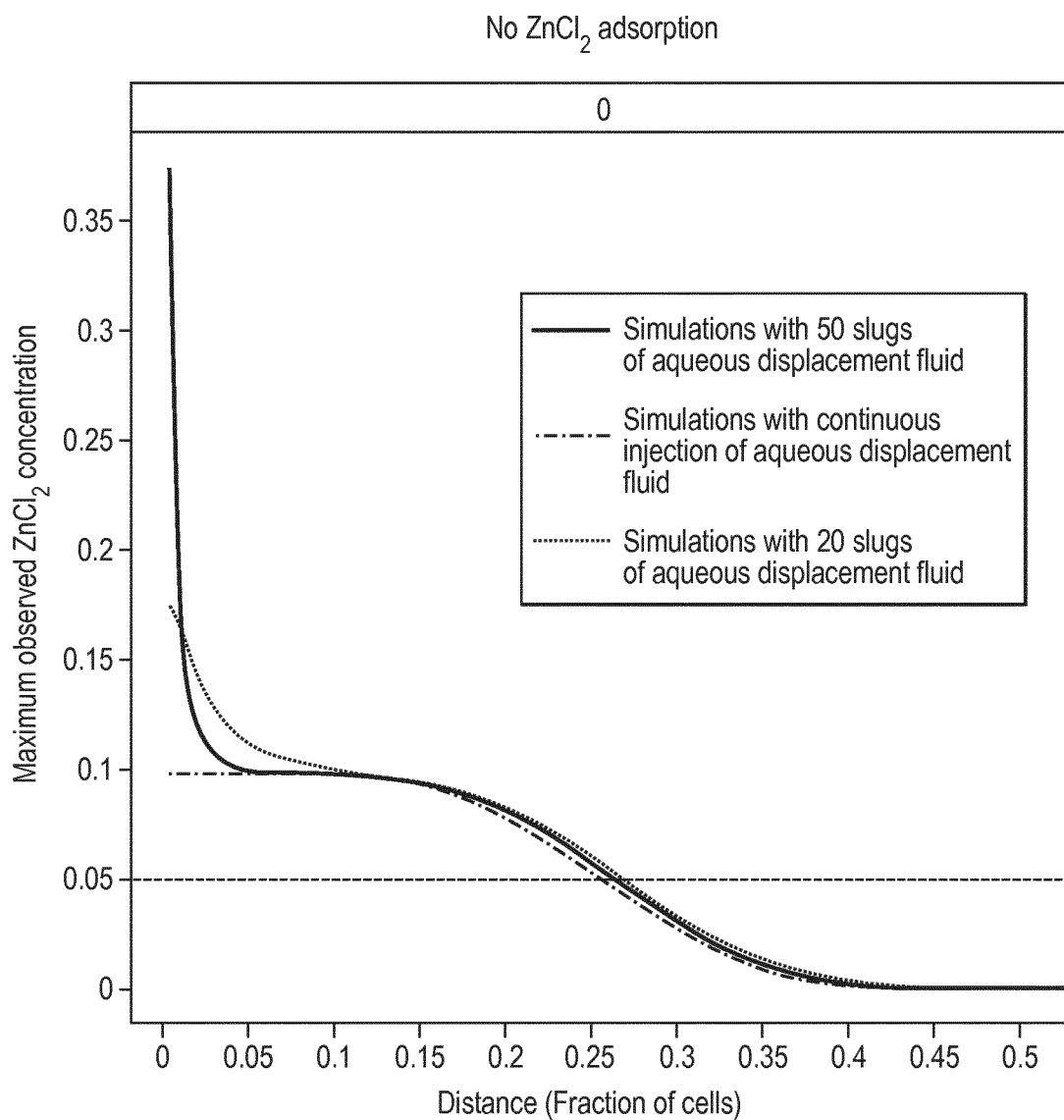


FIG. 1a

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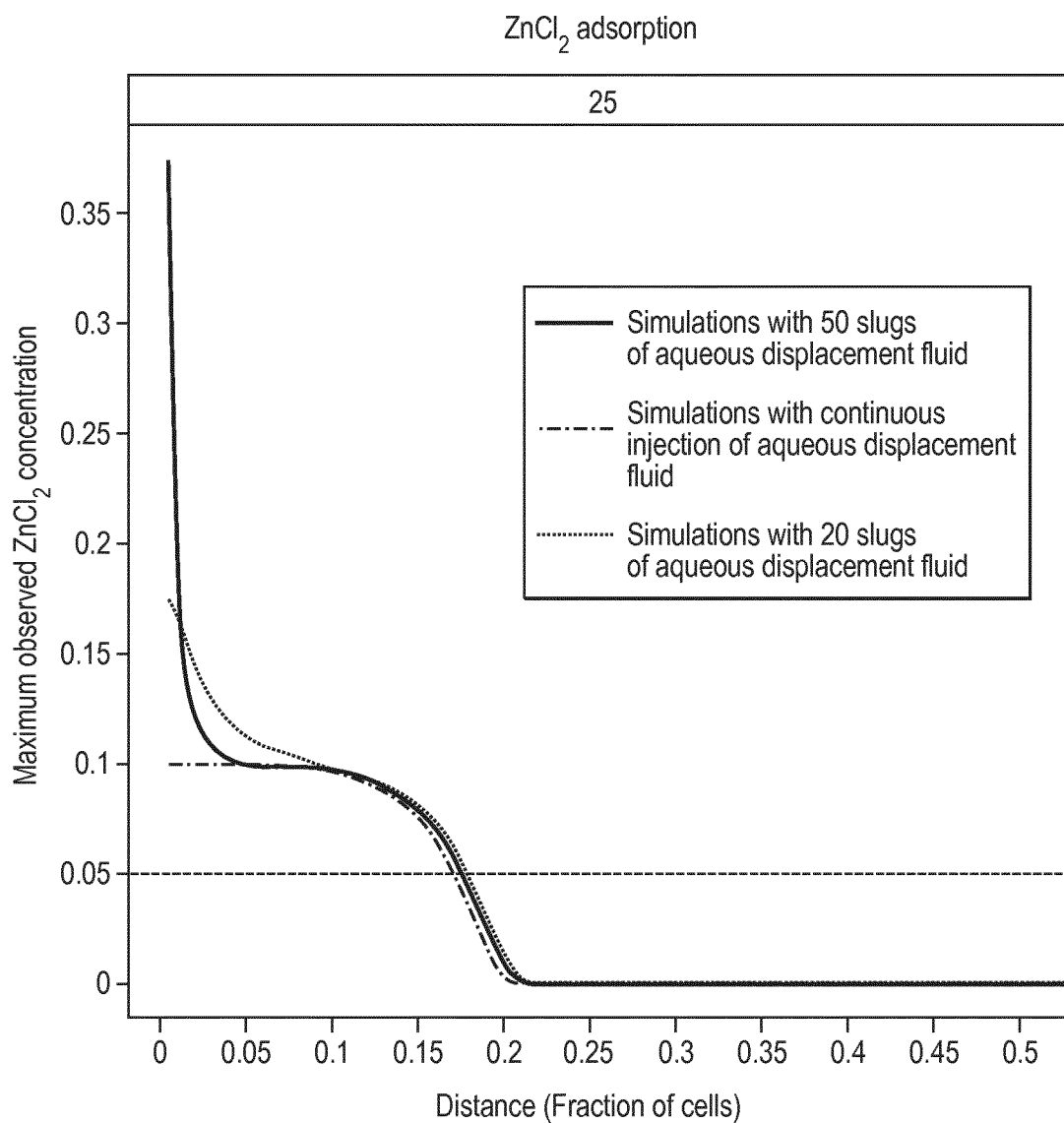


FIG. 1b

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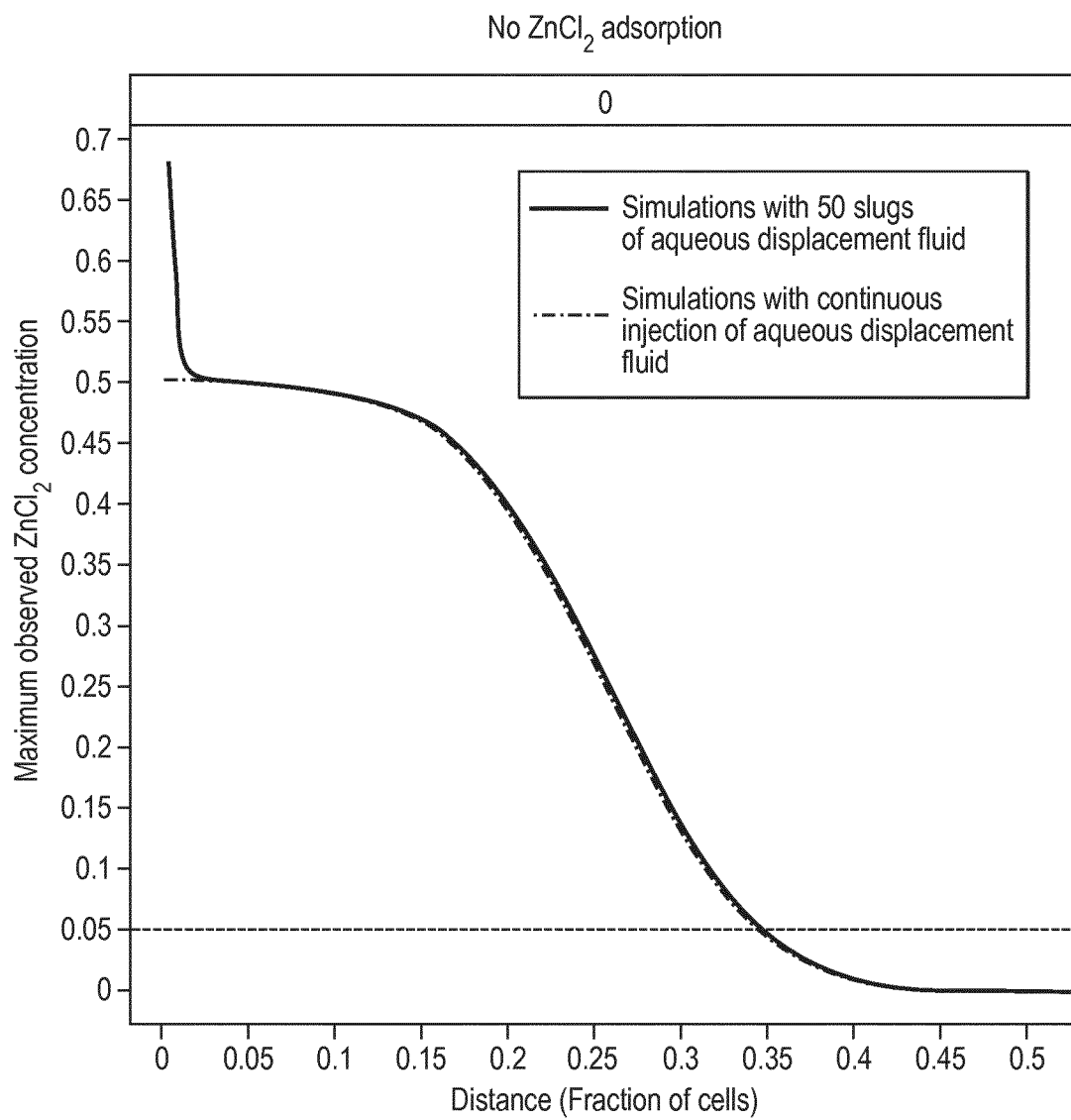


FIG. 2a

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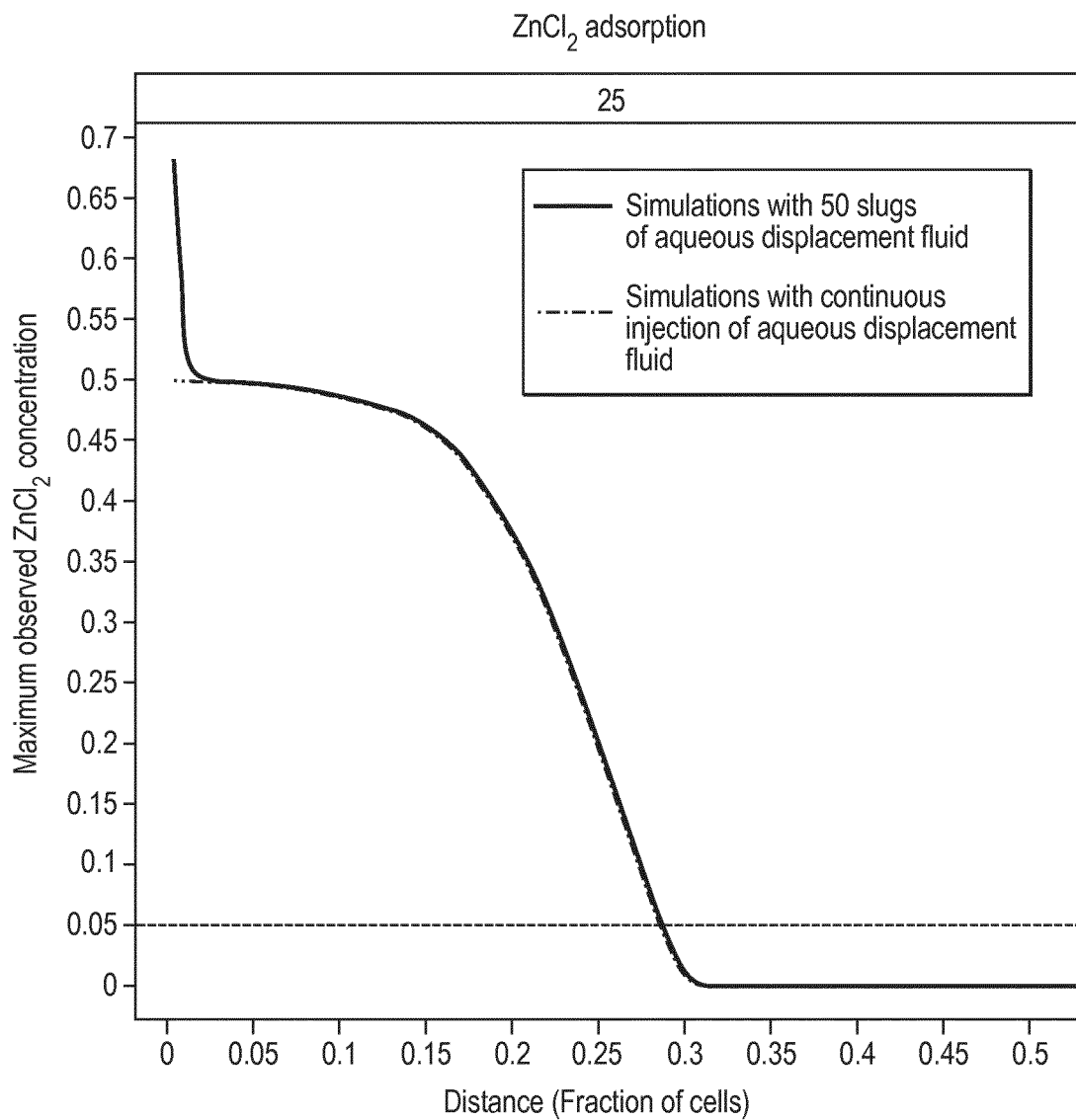


FIG. 2b

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/053804

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/58 E21B43/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K E21B

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

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

EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2015/007749 A1 (BP EXPLORATION OPERATING [GB]; COLLINS IAN RALPH [GB]; LAGER ARNAUD [A]) 22 January 2015 (2015-01-22) pages 1-24; claims; examples -----	1-16
Y	CAO RUIBO ET AL: "Alternative Injection and Its Seepage Mechanism of Polymer Flooding in Heterogeneous Reservoirs", SPE-174586-MS, 1 January 2015 (2015-01-01), XP055478041, DOI: 10.2118/174586-MS ISBN: 978-1-61399-389-7 page 1 - page 11; figures; examples ----- -/-	1-16



Further documents are listed in the continuation of Box C.



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Date of the actual completion of the international search

24 May 2018

Date of mailing of the international search report

04/06/2018

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/053804

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 4 359 093 A (BERNARD GEORGE G) 16 November 1982 (1982-11-16) the whole document -----	1-16

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Information on patent family members

International application No

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