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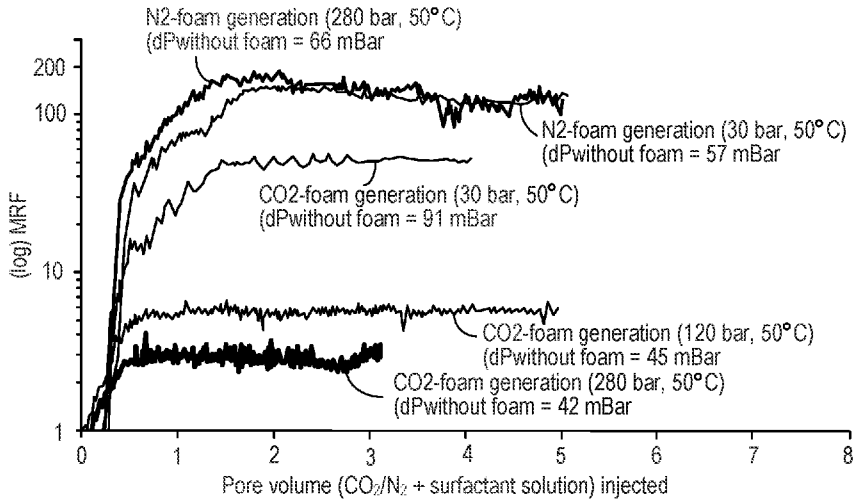


FIG. 2

(57) **Abstract:** Provided are methods of recovering oil from a reservoir using carbon dioxide foam flooding in which a carbon dioxide foam of increased strength is used.

WO 2022/036216 A1

METHOD OF DEPLOYING CARBON DIOXIDE FOAM FLOODING IN AN OIL RESERVOIR

CLAIM OF PRIORITY

[0001] This application claims priority to U.S. Provisional Application No. 63/065,170, filed August 13, 2020, which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] This document relates to a method of oil recovery from a reservoir using carbon dioxide foam flooding, particularly carbon dioxide foam with increased foam strength.

BACKGROUND

[0003] Carbon dioxide (CO_2) flooding can be effective at recovering remaining oil from a reservoir, even one that has already undergone primary depletion and subsequent waterflooding. However, it is common for the CO_2 not to sweep the entire target volume, due to channeling (injectant preferentially sweeping the higher-permeability layers) and gravity override (buoyant CO_2 preferentially sweeps the reservoir's uppermost layers), harming vertical sweep, areal sweep, or both.

[0004] A primary cause of the unfavorable sweep is a condition where the viscosity of the injectant is lower than that of the oil that it is intended to displace. To address this problem, the apparent viscosity of the CO_2 is increased, commonly by foaming the CO_2 in situ. This can be accomplished by alternate injection of slugs of CO_2 and surfactant-laden brine. The surfactant stabilizes foam lamellae in the CO_2 within the rock, adding additional resistance to CO_2 flow. The more stable the lamellae, the more lamellae exist, and the greater the increase in CO_2 apparent viscosity.

[0005] A problem in this usage lies in the inherent weakness of CO_2 foam. The water solubility of CO_2 is much greater than most other enhanced oil recovery (EOR) injectants. This limits the magnitude of the change in pressure (ΔP) that can be maintained across a curved foam lamella, because excessive ΔP leads to diffusion of CO_2 from one side to the other while the lamella stays stationary. This relieves the ΔP, thus providing a mechanism for limiting the magnitude of ΔP across a lamella, which in

turn limits the degree of increase in apparent CO_2 viscosity by foam. This weakness of CO_2 foam results in limited success when used to increase CO_2 sweep. Thus, an improved method is needed for CO_2 foam flooding that results in increased foam strength.

SUMMARY

[0006] Provided in this disclosure is a method for recovering oil from a reservoir. In some embodiments, the method involves: providing a first foam comprising carbon dioxide (CO_2) to the reservoir; providing a second foam to the reservoir, wherein the second foam is produced by alternately injecting into the reservoir: a gas-mixture comprising CO_2 and nitrogen (N_2) or CO_2 and methane (CH_4) or CO_2 and N_2 and CH_4; and a solution comprising brine and a surfactant; and recovering oil from the reservoir.

[0007] In some embodiments of the method, the gas-mixture comprises CO_2 and N_2. In some embodiments, the gas-mixture comprises about 1 mol% to about 99 mol% N_2. In some embodiments, the gas-mixture comprises CO_2 and CH_4. In some embodiments, the gas-mixture comprises about 1 mol% to about 99 mol% CH_4. In some embodiments, the gas-mixture is provided as a slug.

[0008] In some embodiments of the method, the surfactant in the solution comprising brine and a surfactant is selected from a nonionic surfactant, an anionic surfactant, a zwitterionic surfactant, and combinations thereof. In some embodiments, the surfactant comprises about 1% to about 15% of the solution. In some embodiments, the solution comprising brine and a surfactant is provided as a slug.

[0009] In some embodiments of the method, providing the second foam to the reservoir is repeated until the recovery of the oil from the reservoir reaches an economic limit. In some embodiments, providing the second foam to the reservoir is performed one time or more than one time.

[0010] In some embodiments of the method, the first foam is formed in situ in the reservoir. In some embodiments, the first foam is formed by alternately injecting a solution comprising CO_2 and a solution comprising brine and a surfactant. In some embodiments, the solution comprising CO_2 and the solution comprising brine and a surfactant are each provided as slugs. In some embodiments, the alternate injection of the solution comprising CO_2 and the solution comprising brine and a surfactant is repeated until the recovery of the oil from the reservoir reaches an economic limit. In

some embodiments, the alternate injection of the solution comprising CO_2 and the solution comprising brine and a surfactant is performed one time or more than one time.

[0011] In some embodiments, the method comprises injecting a solution comprising N_2 and a solution comprising brine and a surfactant after providing the first foam to the reservoir. In some embodiments, the solution comprising N_2 and a solution comprising brine and a surfactant are injected simultaneously.

[0012] In some embodiments, the method results in a greater apparent viscosity of the CO_2 as compared to a method that does not include the step of providing the second foam to the reservoir. In some embodiments, the method increases the total sweep efficiency of the reservoir as compared to a method that does not include the step of providing the second foam to the reservoir. In some embodiments, the method provides increased oil recovery as compared to a method that does not include the step of providing the second foam to the reservoir.

[0013] Also provided in the present disclosure is a method for flooding a reservoir with CO_2 foam, comprising providing a foam to the reservoir, wherein the foam is produced by alternately injecting into the reservoir: a gas-mixture comprising CO_2 and N_2 or CO_2 and CH_4 or CO_2 and N_2 and CH_4; and a solution comprising brine and a surfactant.

[0014] In some embodiments, the gas-mixture comprises CO_2 and N_2. In some embodiments, the gas-mixture comprises about 1 mol% to about 99 mol% N_2. In some embodiments, the gas-mixture comprises CO_2 and CH_4. In some embodiments, the gas-mixture comprises about 1 mol% to about 90 mol% CH_4. In some embodiments, the gas-mixture is provided as a slug.

[0015] In some embodiments, the surfactant in the solution comprising brine and a surfactant is selected from a nonionic surfactant, an anionic surfactant, a zwitterionic surfactant, and combinations thereof. In some embodiments, the surfactant comprises about 1% to about 15% of the solution. In some embodiments, the solution is provided as a slug.

[0016] In some embodiments of the method, the alternate injections of the gas-mixture and the solution are performed one time or more than one time.

[0017] In some embodiments, the method further comprises injecting into the reservoir a solution comprising N_2 and a solution comprising brine. In some embodiments, the solution comprising N_2 and a solution comprising brine and a

surfactant are injected simultaneously. In some embodiments, the injection of a solution comprising N_2 and a solution comprising brine occurs before the foam is provided to the reservoir. In some embodiments, the injection of a solution comprising N_2 and a solution comprising brine occurs after the foam is provided to the reservoir.

DESCRIPTION OF DRAWINGS

[0018] **FIG. 1** shows the effect of gas composition on foam strength.

[0019] **FIG. 2** shows the effect of pressure on CO_2 foam.

DETAILED DESCRIPTION

[0020] The present disclosure provides methods for recovering oil from a reservoir using carbon dioxide (CO_2) foam flooding. The methods of the present disclosure utilize a CO_2 foam that has been made stronger by dilution with nitrogen (N_2) or methane (CH_4). Methane is less water-soluble than CO_2, and N_2 even less so. Therefore, in some embodiments, CO_2 foam strength increases from a weak foam to a stronger foam by adding CH_4 or N_2. The methods of the present disclosure using the stronger CO_2 foam result in an improved volumetric sweep.

[0021] Additionally, CO_2 has the greatest local displacement efficiency (lowest residual oil saturation (S_{or})), followed by CH_4, with N_2 leaving behind the greatest S_{or}. Thus, in some embodiments, the methods of the present disclosure maximize oil recovery by first allowing CO_2 to sweep as much oil as it can by CO_2 flooding followed by CO_2 foam flooding using the stronger CO_2 foam. In some embodiments, subsequent injection of N_2 along with CO_2 foam enables sweeping of some of the remaining unswept regions, albeit at a higher S_{or}. Thus, the methods of the present disclosure maximize total sweep efficiency of the target reservoir volume. In some embodiments, as the N_2-laden CO_2 front moves through the reservoir, some of the CO_2 partitions from the vapor into the in situ liquid oleic phase. In some embodiments, this results in a leading-edge of the advancing CO_2 -front that is enriched in N_2, which improves sweep even more due to increased foam strength at the propagating foam front. In some embodiments, this method is used in regions of the reservoir unswept by CO_2, where the oil is not yet saturated with CO_2.

[0022] Also provided are methods for improving CO_2 foam processes though generation of a stronger CO_2 foam. In some embodiments, the methods increase CO_2

sweep. In some embodiments, the methods result in greater oil recovery as compared to methods where a CO_2 foam is used that does not contain N_2 or CH_4.

[0023] The methods of the present disclosure can be used in any type of reservoir or underground formation, such as sandstone or carbonate or porous or fractured rock formation.

[0024] Reference will now be made in detail to certain embodiments of the disclosed subject matter. While the disclosed subject matter will be described in conjunction with the enumerated claims, it will be understood that the exemplified subject matter is not intended to limit the claims to the disclosed subject matter.

[0025] **Definitions**

[0026] Values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a range of "about 0.1% to about 5%" or "about 0.1% to 5%" should be interpreted to include not just about 0.1% to about 5%, but also the individual values (for example, 1%, 2%, 3%, and 4%) and the sub-ranges (for example, 0.1% to 0.5%, 1.1% to 2.2%, 3.3% to 4.4%) within the indicated range. The statement "about X to Y" has the same meaning as "about X to about Y," unless indicated otherwise. Likewise, the statement "about X, Y, or about Z" has the same meaning as "about X, about Y, or about Z," unless indicated otherwise.

[0027] In this document, the terms "a," "an," or "the" are used to include one or more than one unless the context clearly dictates otherwise. The term "or" is used to refer to a nonexclusive "or" unless otherwise indicated. The statement "at least one of A and B" has the same meaning as "A, B, or A and B." In addition, it is to be understood that the phraseology or terminology employed in this disclosure, and not otherwise defined, is for the purpose of description only and not of limitation. Any use of section headings is intended to aid reading of the document and is not to be interpreted as limiting; information that is relevant to a section heading may occur within or outside of that particular section.

[0028] In the methods described herein, the acts can be carried out in any order, except when a temporal or operational sequence is explicitly recited. Furthermore, specified acts can be carried out concurrently unless explicit claim language recites that

they be carried out separately. For example, a claimed act of doing X and a claimed act of doing Y can be conducted simultaneously within a single operation, and the resulting process will fall within the literal scope of the claimed process.

[0029] The term "about" as used herein can allow for a degree of variability in a value or range, for example, within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range.

[0030] As used herein, "strong foam" means foam that causes a large reduction in gas viscosity, while "weak foam" means foam that causes only a small reduction in gas viscosity. Stronger foam results in greater improvement in sweep efficiency of the injectant.

[0031] As used herein, the term "sweep efficiency" refers to a measure of the effectiveness of an enhanced oil recovery process. In some embodiments, sweep efficiency is the percentage of the reservoir volume displaced of oil by an injection fluid at a particular time.

[0032] Residual oil saturation (S_{or}) is defined as the fraction of the reservoir pore volume which does not flow.

[0033] **Method for recovering oil from a reservoir**

[0034] Provided in the present disclosure are methods for recovering oil from a reservoir. The methods of the present disclosure are improved methods for flooding a reservoir with CO_2, resulting in increased sweep efficiency, as compared to, for example, standard methods of CO_2 foam flooding. The methods of the present disclosure include: providing a first foam comprising carbon dioxide (CO_2) to the reservoir; providing a second foam to the reservoir, where the second foam is produced by alternately injecting into the reservoir a gas-mixture comprising CO_2 and nitrogen (N_2) or CO_2 and methane (CH_4); and a solution comprising brine and a surfactant; and recovering oil from the reservoir.

[0035] In some embodiments, the methods of the present disclosure result in a greater apparent viscosity of the CO_2 in the foam as compared to a method of CO_2 foam flooding that does not include flooding with a CO_2 foam diluted with either N_2 or CH_4. In some embodiments, the methods of the present disclosure increase the total sweep efficiency of the reservoir as compared to a method of CO_2 foam flooding that does not include flooding with a CO_2 foam diluted with either N_2 or CH_4. In some embodiments, the methods of the present disclosure provide increased oil recovery as compared to a

method of CO_2 foam flooding that does not include flooding with a CO_2 foam diluted with either N_2 or CH_4.

[0036] **CO_2 foam flooding**

[0037] In some embodiments, the first step of the method includes injecting a first foam containing CO_2 into a reservoir or well. For example, the first step can be any method of CO_2 foam flooding used in enhanced oil recovery (EOR) applications known to those skilled in the art. Thus, in some embodiments of the method, the first foam is any CO_2-containing foam that is typically used for foam flooding.

[0038] The foam can be formed in any one of a number of ways. In some embodiments, the foam is generated at the surface by combining the ingredients in a suitable mixing device, such as a foam generator, then injected into the reservoir. In other embodiments, the foam is generated in situ by injecting the ingredients of the foam either separately or simultaneously into the reservoir. In yet other embodiments, two or more of the components are mixed together at the surface prior to introduction into the well, then the foam forms during its passage down the well and in the reservoir in the vicinity of the well.

[0039] In some embodiments of the provided method, the foam is formed in situ in the reservoir. In some embodiments, forming the foam in situ includes alternately injecting a gas-mixture containing CO_2 and a solution containing brine and a surfactant into the reservoir. In some embodiments, the gas-mixture and the solution are each injected as slugs. In further embodiments, the steps of injecting the carbon dioxide slug and the brine and surfactant slug is repeated in alternating fashion to enhance recovery of oil from a reservoir.

[0040] In some embodiments of the method, the alternate injections of the gas-mixture containing CO_2 and the solution containing brine and a surfactant are each performed one time or more than one time. For example, the gas-mixture and the solution can each be injected one time, two times, three times, four times, five times, or more. The number of times the gas-mixture and the solution are injected can depend on any number of factors. For example, the number of times the gas-mixture and the solution are injected can depend on the process design for a specific reservoir. In some embodiments, the number of times the gas-mixture and the solution are injected depends on the availability of surface injection facilities. In some embodiments, the alternate injections are repeated until a foam comprising CO_2 has formed. In some embodiments,

the alternate injections of the gas-mixture containing CO_2 and the solution containing brine and a surfactant are repeated until the recovery of the oil from the reservoir reaches an economic limit. Regarding the economic limit of a well (reservoir) or group of wells, there are costs associated with keeping a well on production, including, but not limited to, artificial lift, surface fluid processing and transport, production testing and monitoring, and well and equipment maintenance. The well (reservoir) or group of wells must not only produce enough valuable fluids, such as oil, to cover all such costs, but also provide an adequate profit for the company. For example, where CO_2 is injected, often a large fraction of the injected CO_2 is produced at the production wells. There is a cost associated with handling these sometimes very large quantities of gas. In other examples, the same reasoning applies to having to handle large amounts of produced water in some wells. The economic limit is the flow rate below which the oil and gas production rates have insufficient value to cover the associated costs and the required profit margin.

[0041] The amount of the carbon dioxide injected into the reservoir will vary for different reservoirs, and will be dependent upon total reservoir pore volume, hydrocarbon pore volume, and other unique reservoir characteristics. In some embodiments, the amount of carbon dioxide injected depends on the effective pore volume, which is the portion of the reservoir which is expected to be contacted by the carbon dioxide injected. Effective pore volume can be determined by conventional laboratory and field techniques known to those of skill in the art.

[0042] The surfactant included in the brine solution can be any surfactant capable of forming a foam with CO_2. In some embodiments, the surfactant is selected from a nonionic surfactant, an anionic surfactant, a zwitterionic surfactant, and combinations thereof.

[0043] **Diluted CO_2 foam flooding**

[0044] In some embodiments, the method includes providing a foam to the reservoir that contains CO_2 diluted with either nitrogen (N_2) or methane (CH_4), or both N_2 and CH_4. Without wishing to be bound by any particular theory, it is believed that CO_2 foam can be made stronger by dilution with small concentrations of N_2 or CH_4. Methane is less water-soluble than CO_2, and N_2 even less so. Therefore, CO_2 foam can increase in strength by adding CH_4 or N_2. Stronger foam can lead to improvement in volumetric sweep.

[0045] In some embodiments of the method, the diluted foam containing CO_2 and either N_2 or CH_4 or both N_2 and CH_4 is provided to the reservoir after providing a first foam containing CO_2 to the reservoir. In some embodiments of the method, the diluted foam containing CO_2 and either N_2 or CH_4 or both N_2 and CH_4 is provided to the reservoir after CO_2 foam flooding has been performed, such as CO_2 foam flooding used in enhanced oil recovery (EOR) applications known to those skilled in the art.

[0046] In some embodiments, the diluted foam containing CO_2 and either N_2 or CH_4 or both N_2 and CH_4 is produced by alternately injecting into the reservoir a gas-mixture containing CO_2 and N_2, a gas-mixture containing CO_2 and CH_4, or a gas mixture containing CO_2, N_2 and CH_4; and a solution containing brine and a surfactant. In some embodiments, the gas-mixture is provided as a slug. In some embodiments, the solution containing brine and a surfactant is provided as a slug.

[0047] In some embodiments, the gas-mixture contains CO_2 and N_2. The gas-mixture can contain an amount of N_2 that is sufficient to increase the strength of the foam once formed. In some embodiments, the gas-mixture contains about 1 mol% to about 99 mol% N_2, for example, about 1 mol% to about 90 mol%, about 10 mol% to about 80 mol%, about 20 mol% to about 70 mol%, about 30 mol% to about 60 mol%, or about 50 mol% N_2. In some embodiments, the gas-mixture contains about 1 mol%, about 5 mol%, about 10 mol%, about 15 mol%, about 20 mol%, about 25 mol%, about 30 mol%, about 35 mol%, about 40 mol%, about 45 mol%, about 50 mol%, about 55 mol%, about 60 mol%, about 65 mol%, about 70 mol%, about 75 mol%, about 80 mol%, about 85 mol%, about 90 mol%, about 95 mol%, or about 99 mol% N_2.

[0048] In some embodiments, the gas-mixture contains CO_2 and CH_4. The gas-mixture can contain an amount of CH_4 that is sufficient to increase the strength of the foam once formed. In some embodiments, the gas-mixture contains about 1 mol% to about 99 mol% CH_4, for example, about 1 mol% to about 90 mol%, about 10 mol% to about 80 mol%, about 20 mol% to about 70 mol%, about 30 mol% to about 60 mol%, or about 50 mol% CH_4. In some embodiments, the gas-mixture contains about 1 mol%, about 5 mol%, about 10 mol%, about 15 mol%, about 20 mol%, about 25 mol%, about 30 mol%, about 35 mol%, about 40 mol%, about 45 mol%, about 50 mol%, about 55 mol%, about 60 mol%, about 65 mol%, about 70 mol%, about 75 mol%, about 80 mol%, about 85 mol%, about 90 mol%, about 95 mol%, or about 99 mol% CH_4.

[0049] In some embodiments, the gas-mixture contains CO_2 and both N_2 and CH_4. The gas-mixture can contain a total amount of N_2 and CH_4 that is sufficient to increase the strength of the foam once formed. In some embodiments, the gas-mixture contains about 1 mol% to about 99 mol% N_2 and CH_4, for example, about 1 mol% to about 90 mol%, about 10 mol% to about 80 mol%, about 20 mol% to about 70 mol%, about 30 mol% to about 60 mol%, or about 50 mol% N_2 and CH_4. In some embodiments, the gas-mixture contains about 1 mol%, about 5 mol%, about 10 mol%, about 15 mol%, about 20 mol%, about 25 mol%, about 30 mol%, about 35 mol%, about 40 mol%, about 45 mol%, about 50 mol%, about 55 mol%, about 60 mol%, about 65 mol%, about 70 mol%, about 75 mol%, about 80 mol%, about 85 mol%, about 90 mol%, about 95 mol%, or about 99 mol% N_2 and CH_4.

[0050] The amount of the gas-mixture containing carbon dioxide and either N_2 or CH_4 or both N_2 and CH_4 injected into the reservoir will vary for different reservoirs, and will be dependent upon total reservoir pore volume, hydrocarbon pore volume, reservoir fluid composition and other unique reservoir characteristics. In some embodiments, the amount of carbon dioxide injected depends on the effective pore volume, which is the portion of the reservoir which is expected to be contacted by the carbon dioxide injected. Effective pore volume can be determined by conventional laboratory and field techniques known to those of skill in the art.

[0051] The surfactant included in the brine solution can be any surfactant capable of forming a foam with CO_2. In some embodiments, the surfactant is selected from a nonionic surfactant, an anionic surfactant, a zwitterionic surfactant, and combinations thereof. Suitable surfactants include, but are not limited to a cocamidopropyl betaine surfactant (for example, Amphosol®, sold by Stepan Company, Northfield, IL, USA), sodium dodecyl sulfonate, and selected anionic, cationic, zwitterionic or optimized proprietary blends of many surfactants.

[0052] In some embodiments, the solution contains about 0.1% to about 5% of the surfactant, such as about 0.1% to about 4%, about 0.5% to about 3%, about 1% to about 2%, or about 0.1%, about 0.2%, about 0.3%, about 0.4%, about 0.5%, about 0.6%, about 0.7%, about 0.8%, about 0.9%, about 1%, about 1.5%, about 2%, about 2.5%, about 3%, about 3.5%, about 4%, about 4.5%, or about 5% surfactant.

[0053] In some embodiments of the method, the alternate injections of the gas-mixture containing CO_2 and either N_2 or CH_4 or both N_2 and CH_4 and the solution

containing brine and a surfactant are each performed one time or more than one time. For example, the gas-mixture and the solution can each be injected one time, two times, three times, four times, five times, or more. In some embodiments, the alternate injections are repeated until a foam has formed. In some embodiments, the alternate injections of the gas-mixture and the solution are repeated until the recovery of the oil from the reservoir reaches an economic limit.

[0054] ***N_2 foam injection***

[0055] In some embodiments of the method, the method further includes a step of injecting an N_2 foam into the reservoir. In some embodiments, the N_2 foam is formed by injecting a solution containing N_2 and a solution containing brine and a surfactant into the reservoir. In some embodiments, the solution containing N_2 and the solution containing brine and a surfactant are injected simultaneously. In some embodiments, the solution containing N_2 and the solution containing brine and a surfactant are injected sequentially. In some embodiments, the solution containing N_2 is injected first, followed by injection of the solution containing brine and a surfactant. In some embodiments, the N_2 foam is provided as a slug.

[0056] In some embodiments, the N_2 foam is provided to the reservoir prior to providing the diluted foam containing CO_2 and either N_2 or CH_4 or both N_2 and CH_4. In some embodiments of the method, the N_2 foam is provided to the reservoir after providing a first foam containing CO_2 to the reservoir. In some embodiments of the method, the N_2 foam is provided to the reservoir after CO_2 foam flooding has been performed, such as CO_2 foam flooding used in enhanced oil recovery (EOR) applications known to those skilled in the art. Without wishing to be bound by any theory, it is believed that because CO_2 has a higher local displacement efficiency (lowest residual oil saturation (S_{or})) than N_2, allowing CO_2 to first sweep as much oil from the reservoir by CO_2 foam flooding, the subsequent injection of the N_2 foam enables improved volumetric sweeping of the remaining unswept regions, albeit at a higher S_{or}, thus maximizing total sweep efficiency of the target reservoir volume.

[0057] **Method for flooding a reservoir**

[0058] Also provided in the present disclosure are methods for flooding a reservoir with diluted CO_2 foam, such as the diluted foam provided herein. In some embodiments, the foam is diluted with N_2. In some embodiments, the foam is diluted with methane. In some embodiments, the foam is diluted with both N_2 and methane. The method includes

providing a foam to a reservoir, where the foam is produced by alternately injecting into the reservoir a gas-mixture containing CO_2 and N_2 or CO_2 and CH_4 or CO_2 and N_2 and CH_4; and a solution comprising brine and a surfactant. In some embodiments, the gas-mixture is provided as a slug. In some embodiments, the solution is provided as a slug.

[0059] In some embodiments of the method, the alternate injections of the gas-mixture containing CO_2 and either N_2 or CH_4 or both N_2 and CH_4 and the solution containing brine and a surfactant are each performed one time or more than one time. For example, the gas-mixture and the solution can each be injected one time, two times, three times, four times, five times, or more. In some embodiments, the alternate injections are repeated until a foam has formed. In some embodiments, the alternate injections of the gas-mixture and the solution are repeated until the recovery of the oil from the reservoir reaches an economic limit.

[0060] In some embodiments of the method, the method further includes a step of injecting an N_2 foam into the reservoir. In some embodiments, the N_2 foam is formed by injecting a solution containing N_2 and a solution containing brine and a surfactant into the reservoir. In some embodiments, the solution containing N_2 and the solution containing brine and a surfactant are injected simultaneously. In some embodiments, the solution containing N_2 and the solution containing brine and a surfactant are injected sequentially. In some embodiments, the solution containing N_2 is injected first, followed by injection of the solution containing brine and a surfactant. In some embodiments, the N_2 foam is provided as a slug.

[0061] In some embodiments, the N_2 foam is provided to the reservoir prior to providing the diluted foam containing CO_2 and either N_2 or CH_4 or both N_2 and CH_4. In some embodiments, the N_2 foam is provided to the reservoir after providing the diluted foam containing CO_2 and either N_2 or CH_4 or both N_2 and CH_4.

[0062] Thus, also provided are methods for increasing sweep efficiency using the diluted CO_2 foam containing either N_2 or CH_4 or both N_2 and CH_4.

[0063] **Other Applications**

[0064] The methods of the present disclosure can be used in any subterranean formation or reservoir where oil recovery is desired. For example, the methods can be used to recover remaining oil from a reservoir that has already undergone primary depletion and subsequent waterflooding. The methods can be used to produce oil from a reservoir after secondary or tertiary production methods have been performed. The

methods of the present disclosure can be used in carbonate formations or sandstone formations.

[0065] **EXAMPLES**

[0066] Laboratory flooding experiments of reservoir core plug samples were conducted to demonstrate the effects of gas composition on foam in porous media. Foams containing different gases (N_2, flue gas (a mixture of 20 mol% CO_2 and 80 mol% N_2 emitted as exhaust from power plants), CH_4, CO_2, and a mixture of CO_2 and CH_4 (50/50 mol%)) were prepared and the strength of the foam was tested across a pressure gradient, as described in Zeng *et al.*, Langmuir, 32:6239-6245 (2016). FIG. 1 displays the apparent viscosity of foam of different compositions at low pressures (greater pressure gradient means greater apparent viscosity). At low pressure conditions, CO_2 was a weaker foam, with CH_4 twice as strong and N_2 three times as strong. Mixing CO_2 with other gases resulted in a foam as strong as the other gases alone. Since CO_2 becomes more water-soluble at higher pressures, the CO_2 foam became much weaker. As shown in FIG. 2, at 30 bar CO_2 foam was only 5x weaker than N_2, while at 280 bar CO_2 foam was 100x weaker (note the logarithmic scale on the graph). See also Solbakken et al., Ph.D. dissertation, University of Bergen (2015).

[0067] Because many CO_2 floods occur at the higher reservoir pressures, this shows that diluting the injected CO_2 with other gases, such as N_2 or CH_4, at reservoir conditions can increase foam strength.

[0068] **OTHER EMBODIMENTS**

[0069] It is to be understood that while the invention has been described in conjunction with the detailed description thereof, the foregoing description is intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims. Other aspects, advantages, and modifications are within the scope of the following claims.

WHAT IS CLAIMED IS:

1. A method for recovering oil from a reservoir, comprising:

providing a first foam comprising carbon dioxide (CO_2) to the reservoir;

providing a second foam to the reservoir, wherein the second foam is produced by alternately injecting into the reservoir:

a gas-mixture comprising CO_2 and nitrogen (N_2) or CO_2 and methane (CH_4) or CO_2 and N_2 and CH_4; and

a solution comprising brine and a surfactant; and

recovering oil from the reservoir.

2. The method of claim 1, wherein the gas-mixture comprises CO_2 and N_2.

3. The method of claim 2, wherein the gas-mixture comprises about 1 mol% to about 99 mol% N_2.

4. The method of claim 1, wherein the gas-mixture comprises CO_2 and CH_4.

5. The method of claim 4, wherein the gas-mixture comprises about 1 mol% to about 99 mol% CH_4.

6. The method of claim 1, wherein the gas-mixture is provided as a slug.

7. The method of claim 1, wherein the surfactant is selected from a nonionic surfactant, an anionic surfactant, a zwitterionic surfactant, and combinations thereof.

8. The method of claim 1, wherein the surfactant comprises about 1% to about 15% of the solution.

9. The method of claim 1, wherein the solution is provided as a slug.

10. The method of claim 1, wherein providing the second foam to the reservoir is repeated until the recovery of the oil from the reservoir reaches an economic limit.

11. The method of claim 1, wherein providing the second foam to the reservoir is performed one time or more than one time.

12. The method of claim 1, wherein the first foam is formed in situ in the reservoir.

13. The method of claim 12, wherein the first foam is formed by alternately injecting a solution comprising CO_2 and a solution comprising brine and a surfactant.

14. The method of claim 13, wherein the solution comprising CO_2 and the solution comprising brine and a surfactant are each provided as slugs.

15. The method of claim 13, wherein the alternate injection of the solution comprising CO_2 and the solution comprising brine and a surfactant is repeated until the recovery of the oil from the reservoir reaches an economic limit.

16. The method of claim 13, wherein the alternate injection of the solution comprising CO_2 and the solution comprising brine and a surfactant is performed one time or more than one time.

17. The method of claim 1, wherein the method comprises injecting a solution comprising N_2 and a solution comprising brine and a surfactant after providing the first foam to the reservoir.

18. The method of claim 17, wherein the solution comprising N_2 and a solution comprising brine and a surfactant are injected simultaneously.

19. The method of claim 1, wherein the method results in a greater apparent viscosity of the CO_2 as compared to a method that does not include the step of providing the second foam to the reservoir.

20. The method of claim 1, wherein the method increases the total sweep efficiency of the reservoir as compared to a method that does not include the step of providing the second foam to the reservoir.

21. The method of claim 1, wherein the method provides increased oil recovery as compared to a method that does not include the step of providing the second foam to the reservoir.

22. A method for flooding a reservoir with CO_2 foam, comprising providing a foam to the reservoir, wherein the foam is produced by alternately injecting into the reservoir:

a gas-mixture comprising CO_2 and nitrogen (N_2) or CO_2 and methane (CH_4) or CO_2 and N_2 and CH_4; and

a solution comprising brine and a surfactant.

23. The method of claim 22, wherein the gas-mixture comprises CO_2 and N_2.

24. The method of claim 23, wherein the gas-mixture comprises about 1 mol% to about 99 mol% N_2.

25. The method of claim 22, wherein the gas-mixture comprises CO_2 and CH_4.

26. The method of claim 25, wherein the gas-mixture comprises about 1 mol% to about 90 mol% CH_4.

27. The method of claim 22, wherein the gas-mixture is provided as a slug.

28. The method of claim 22, wherein the surfactant is selected from a nonionic surfactant, an anionic surfactant, a zwitterionic surfactant, and combinations thereof.

29. The method of claim 22, wherein the surfactant comprises about 1% to about 15% of the solution.

30. The method of claim 22, wherein the solution is provided as a slug.

31. The method of claim 22, wherein the alternate injections of the gas-mixture and the solution are performed one time or more than one time.

32. The method of claim 22, wherein the method further comprises injecting into the reservoir a solution comprising N_2 and a solution comprising brine.

33. The method of claim 32, wherein the solution comprising N_2 and a solution comprising brine and a surfactant are injected simultaneously.

34. The method of claim 32, wherein the injection of a solution comprising N_2 and a solution comprising brine occurs before the foam is provided to the reservoir.

35. The method of claim 32, wherein the injection of a solution comprising N_2 and a solution comprising brine occurs after the foam is provided to the reservoir.

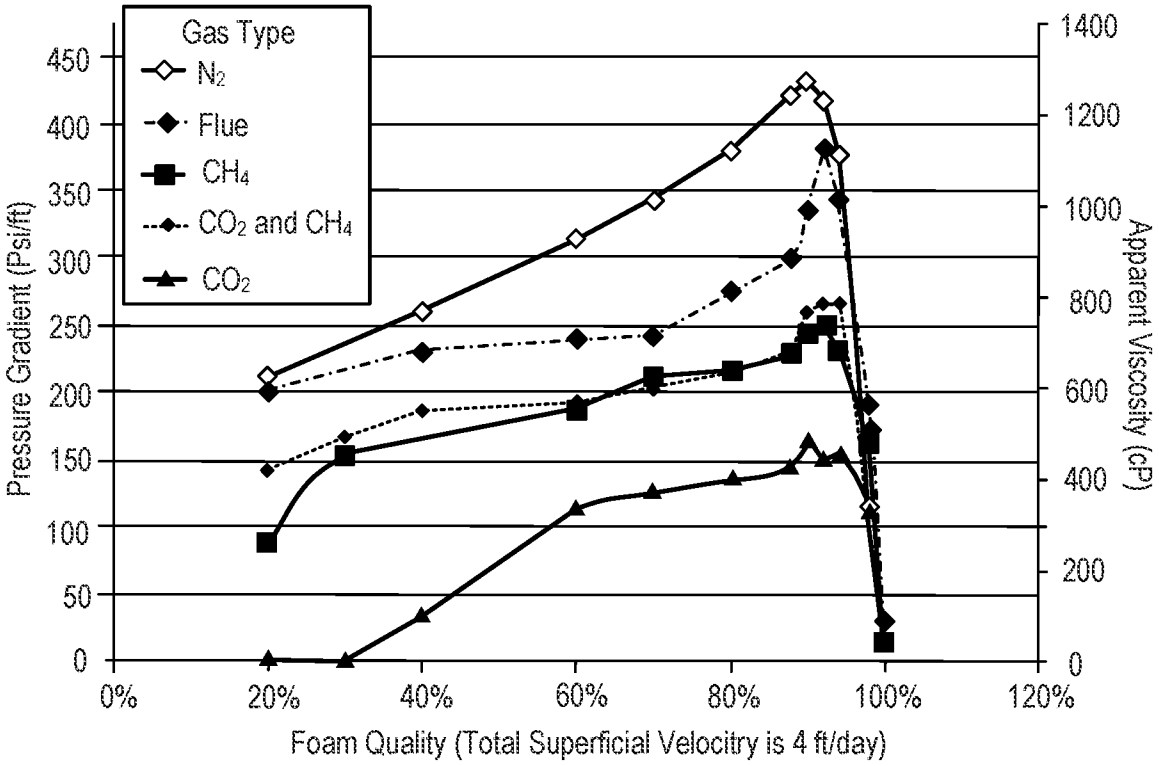

Gas Type
N2
Flue
CH4
CO2 and CH4
CO2
Pressure Gradient (Psi/ft)
Apparent Viscosity (cP)
Foam Quality (Total Superficial Velocitry is 4 ft/day)
0
50
100
150
200
250
300
350
400
450
0%
20%
40%
60%
80%
100%
120%
200
400
600
800
1000
1200
1400

FIG. 1

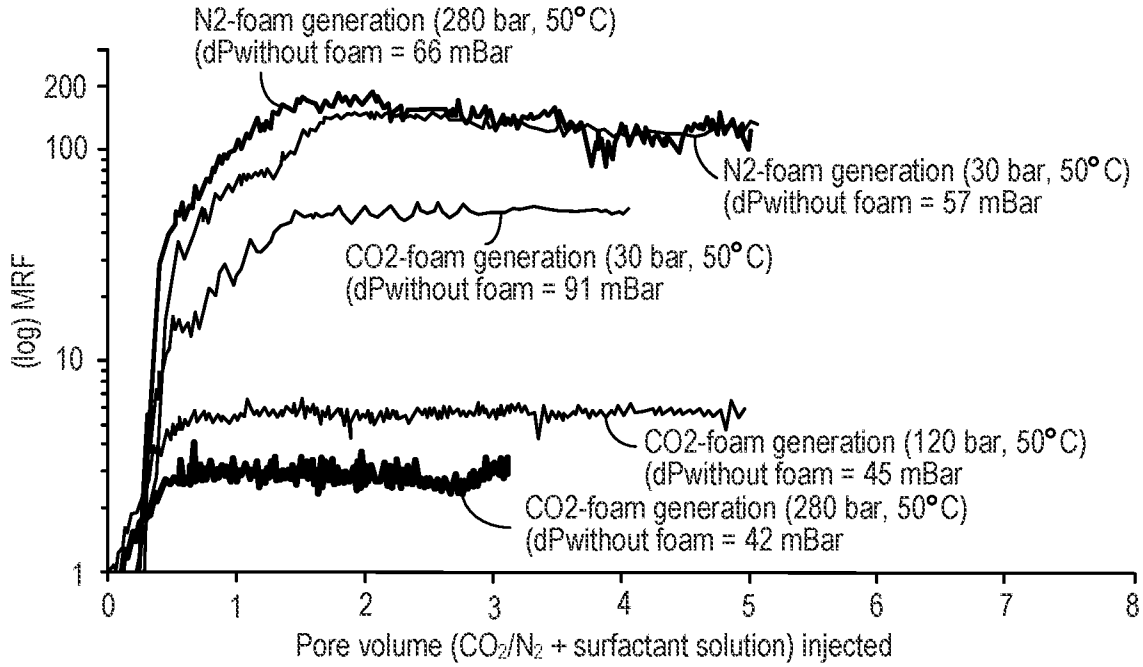

N2-foam generation (280 bar, 50°C)
(dPwithout foam = 66 mBar
N2-foam generation (30 bar, 50°C)
(dPwithout foam = 57 mBar
CO2-foam generation (30 bar, 50°C)
(dPwithout foam = 91 mBar
CO2-foam generation (120 bar, 50°C)
(dPwithout foam = 45 mBar
CO2-foam generation (280 bar, 50°C)
(dPwithout foam = 42 mBar
(log) MRF
Pore volume (CO2/N2 + surfactant solution) injected
1
10
100
200
0
1
2
3
4
5
6
7
8

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2021/045938

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/594
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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZENG YONGCHAO ET AL: "Role of Gas Type on Foam Transport in Porous Media", LANGMUIR, vol. 32, no. 25, 28 June 2016 (2016-06-28) , pages 6239-6245, XP055860911, US ISSN: 0743-7463, DOI: 10.1021/acs.langmuir.6b00949 Retrieved from the Internet: URL:https://pubs.acs.org/doi/pdf/10.1021/acs.langmuir.6b00949> cited in the application page 6239 - page 6241 page 6244; figure 4 -----	1-35
X	US 4 113 011 A (BERNARD GEORGE G ET AL) 12 September 1978 (1978-09-12) claims 12,17,18; examples 1-3; table 1 ----- -/--	1-35

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 November 2021	26/11/2021

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2021/045938

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 828 032 A (TELETZKE GARY F [US] ET AL) 9 May 1989 (1989-05-09) column 9, lines 2-8; claim 1	1-35
A	SIDDIQUI MOHAMMED ABDUL QADEER ET AL: "Stability and texture of CO2/N2foam in sandstone", COLLOIDS AND SURFACES A: PHYSIOCHEMICAL AND ENGINEERING ASPECTS, vol. 534, 24 May 2017 (2017-05-24), pages 26-37, XP085279344, ISSN: 0927-7757, DOI: 10.1016/J.COLSURFA.2017.04.049 page 27; table 1	1-35
A	SZABRIES MARTINA ET AL: "Foam Analysis at Elevated Pressures for Enhanced Oil Recovery Applications", ENERGY & FUELS, vol. 33, no. 5, 16 May 2019 (2019-05-16), pages 3743-3752, XP055860929, WASHINGTON, DC, US. ISSN: 0887-0624, DOI: 10.1021/acs.energyfuels.8b03088 Retrieved from the Internet: URL:https://pubs.acs.org/doi/pdf/10.1021/acs.energyfuels.8b03088> abstract; figures 6,8	1-35

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2021/045938

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4113011 A	12-09-1978	CA 1089212 A	11-11-1980
		US 4113011 A	12-09-1978
US 4828032 A	09-05-1989	NONE	