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### Surfactant mixtures for enhanced oil recovery

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#### Abstract

A system and a method for making and using an enhanced oil recovery (EOR) fluid. The EOR fluid includes a base fluid, an anionic-nonionic surfactant including one of sodium alkylphenol ethoxylate carboxylate (APEC), sodium alkyl ethoxylate carboxylate (AEC), sodium alkylphenol ethoxylate sulfate (APES), or sodium alkyl ethoxylate sulfate (AES), and a second surfactant including a cationic surfactant including an alkyl pyridine salt.

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## **Background/Summary**

## TECHNICAL FIELD

(1) This disclosure relates to methods of producing oil using a surfactant blend to assist in enhanced oil recovery.

## BACKGROUND

(2) Surfactants are widely used in enhanced oil recovery to aid in displacing fluid and increase the oil recovery for mature fields. The main function of the surfactant is to reduce the interfacial tension (IFT) between crude oil and an injected fluid to ultra-low levels. This increases the capillary number indicating high oil production potential. However, the properties of surfactants are affected by salinity and temperature. Usually, a surfactant-based formulation only fits a narrow range of reservoir conditions in terms of temperature and salinity. Beyond this range, the IFT may increase, lowering oil production. As a result, different surfactant formulations are used for different reservoir conditions to achieve ultra-low IFT to improve oil recovery.

## SUMMARY

(3) An embodiment described herein provides a method for enhanced oil recovery using a surfactant blend in an enhanced oil recovery (EOR) fluid. The method includes preparing the surfactant blend in a base fluid, by adding a first surfactant including a anionic-nonionic surfactant selected from sodium alkylphenol ethoxylate carboxylate (APEC), sodium alkyl ethoxylate carboxylate (AEC), sodium alkylphenol ethoxylate sulfate (APES), or sodium alkyl ethoxylate sulfate (AES), to the base fluid, and adding a second surfactant including a cationic surfactant including an alkyl pyridine salt to the base fluid forming the EOR fluid. The EOR fluid is injected into a reservoir through an injection well. Fluid is pushed to a production well. Fluid is produced from the production well, wherein the produced fluid includes hydrocarbons.

(4) Another embodiment described herein provides an enhanced oil recovery (EOR) fluid. The EOR fluid includes a base fluid, an anionic-nonionic surfactant including one of sodium alkylphenol ethoxylate carboxylate (APEC), sodium alkyl ethoxy late carboxylate (AEC), sodium alkylphenol ethoxylate sulfate (APES), or sodium alkyl ethoxylate sulfate (AES), to the base fluid, and a second surfactant including a cationic surfactant including an alkyl pyridine salt.

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## Description

### BRIEF DESCRIPTION OF DRAWINGS

(1) FIG. 1 is a drawing of an enhanced oil recovery (EOR) process **100**.

(2) FIG. 2 is a process flow diagram of a method **200** for using a surfactant mixture in enhanced oil recovery.

(3) FIG. 3 is a plot of the IFT of 0.2% APEC/CPB at 90° C. in seawater at different mixing ratios.

(4) FIG. 4 is a plot of the IFT of a 0.2% APEC/CPB mixture in the base fluid at a 3/1 ratio of APEC/CPB versus temperatures in brines with different salinities.

### DETAILED DESCRIPTION

(5) This invention provides surfactant mixtures composed of anionic-nonionic surfactant and cationic surfactant for chemical enhanced oil recovery in reservoirs with a wide range of temperatures and salinities. The anionic-nonionic surfactant contains both anionic and nonionic groups in one molecule. Usually, different reservoir conditions require different surfactant formulations to achieve ultra-low oil/water interfacial tension (IFT) to mobilize the residual oil since surfactant properties are affected by the reservoir condition such as salinity and temperature.

(6) The surfactant formulations provided herein examples herein have low IFT of 10.sup.-2 to 10.sup.-3 mN/m under different conditions with different salinities and temperatures. Thus, these surfactant mixtures could be used in reservoirs with different conditions. The IFT of the anionic-nonionic surfactant or the cationic surfactant showed a high IFT, for example, greater than about 0.4 milliNewtons per meter. The low IFT of the mixture of these two surfactants is due to the

synergism between oppositely charged anionic and cationic head groups, which leads to a close packing adsorption layer on the interface. The surfactant mixtures present a significant improvement in oil recovery for reservoirs with different temperatures and salinities due to the increase in ultra-low IFT.

(7) FIG. 1 is a drawing of an enhanced oil recovery (EOR) process **100**. In the EOR process **100**, a mixing system **102** is used to mix the base fluid with a surfactant blend. The mixing system **102** can include pumps, tanks, valves, and other equipment to make the mixture. In various embodiments, the mixing system **102** includes storage tanks for the base fluid, the first surfactant, and the second surfactant. Pumps are then used to add the base fluid, a first surfactant, and the second surfactant to a mixing tank forming the EOR fluid **104**.

(8) A pump injects the EOR fluid **104** into a reservoir **106** through an injection well **108**. For example, the reservoir **106** can be formed by a cap rock layer **110** trapping hydrocarbons over an aquifer **112**, among others. Early in the production from the reservoir **106**, the pressure in the reservoir **106** may be sufficient to force the hydrocarbons to the surface **114** through a production well **116**. However, over time the pressure in the reservoir **106** will decrease, decreasing the production from the reservoir **106**.

(9) In the EOR process **100**, the EOR fluid **104** forces fluids **118** to the production well **116**. The fluids **118** are then produced to the surface **114** through the production well **116**. The fluids **118** may include mixtures of hydrocarbons with entrained water, termed a water cut. The ratio of hydrocarbons to water may be about 100/0, about 90/10, about 70/30, or about 60/40, or lower.

(10) At the surface **114**, the fluids **118** are processed in a separation system **120**, such as a water oil separation plant (WOSP), a water gas separation plant (WGSP), or a combined plant, forming a hydrocarbon stream **122**. The hydrocarbon stream **122** is then sent for further processing, for example, being pumped through a pipeline to a refinery or gas plant.

(11) A water stream **124** from the separation system **120** can be provided to a purification system **126**, which can separate out any remaining hydrocarbons, and determine the concentration of the remaining surfactants. The purification system **126** can include analyzers, pumps, tanks, and the like. Hydrocarbons separated out by the purification system **126** can be returned to the separation system **120** to be combined with the hydrocarbon stream **122**.

(12) A base fluid stream **128** can be provided from the purification system **126** to the mixing system **102**. The base fluid stream **128** can provide at least a portion of the base fluid used for preparing the EOR fluid **104**.

(13) FIG. 2 is a process flow diagram of a method **200** for using a surfactant mixture in enhanced oil recovery. The method begins at block **202** with the preparation of the surfactant blend. In some embodiments, the surfactant blend is made directly in the base fluid, either before or after adding additional ingredients, forming the EOR fluid.

(14) As described herein, the surfactant blend includes two types of surfactants, anionic-nonionic surfactants and cationic surfactants. The anionic-nonionic surfactants include sodium alkylphenol ethoxylate carboxylate (APEC), sodium alkyl ethoxylate carboxylate (AEC), sodium alkylphenol ethoxylate sulfate (APES) and sodium alkyl ethoxylate sulfate (AES). The nonionic group in the anionic surfactant could be ethylene oxide chains, propylene oxide chains, or a mixture of them. The cationic surfactant is an alkyl pyridine salt, such as dodecyl pyridine bromide (DPB), cetylpridinium bromide (CPB), and the like.

(15) In some embodiments, the base fluid is an aqueous fluid, such as a brine. In various embodiments, the salinity of the brine is in a range of about 1000 ppm to about 100,000 ppm, or about 10,000 ppm to about 90,000 ppm, or about 14,000 ppm to about 87,000 ppm, or about 14,420 ppm to about 86,505 ppm. In some embodiments, the salinity is about 10,000 ppm, about 14,420 ppm, about 14,500 ppm, about 20,000 ppm, or about 57,000 ppm, about 57,670 ppm, or about 86,505 ppm. The hardness of the base fluid may range from about 50 ppm to about 5000 ppm, or about 1000 ppm to about 4000 ppm, or about 2000 ppm to about 3000 ppm. In some

embodiments, the hardness of the base fluid is about 500 ppm, or about 2000 ppm, or about 2500 ppm, or about 2760 ppm.

(16) In embodiments described herein, the anionic-nonionic surfactant is in a blend with the cationic surfactant, which provides better solubility than the anionic-nonionic surfactant alone in brine or water, while maintaining a low surface tension. The mixing ratio of the anionic-nonionic surfactant and the cationic surfactant is between about 9:1 to 1:9. In various embodiments, the mixing ratio is about 9:1, or about 3:1, or about 2:1, or about 2:3, or about 1 to 1, or about 1:2, or about 1:3, or about 1:4, or about 1:9. The total concentration of the surfactant blend in the base fluid varies from about 0.01 wt. % to about 1 wt. %. In various embodiments, the total concentration of the surfactant blend is about 0.01 wt. %, about 0.05 wt. %, about 0.1 wt. %, about 0.3 wt. %, about 0.5 wt. %, about 0.75 wt. %, or about 1.0 wt. %. In various embodiments, the total concentration of the surfactant blend is 0.2 wt. %.

(17) The surfactant blend can be used in a temperature range from about 15° C. to about 100° C., from about 40° C. to about 95° C., or from about 50° C. to about 90° C. In various embodiments, the formulation is used at a temperature of about 90° C.

(18) If the surfactant blend has not been prepared in the base fluid, at block **204**, the surfactant blend is added to the base fluid to form the EOR fluid. Additional production chemicals may be added to the EOR fluid to assist in the process. These may be added to the EOR fluid before or after the addition of the surfactants. The base fluid can be water, brine, or an emulsion of oil and brine, for example, including some amount of oil in a recycled water stream from a water oil separation plant. In various embodiments, the amount of oil is less than about 5 vol. %, less than about 2.5 vol. %, less than about 1 vol. %, less than about 0.5 vol. %, less than about 0.1 vol. %, or less than about 1000 ppm. The production chemicals can include a viscosifier, a biocide, an acid, a pH buffer, or any combinations thereof. In some embodiments, the viscosifier is a polysaccharide, such as guar gum, hydroxymethyl cellulose, and the like.

(19) At block **206**, the EOR fluid is injected into a reservoir through an injection well. In various embodiments, multiple injection wells are used. The injection of the EOR fluid forces fluid proximate to the injection well through the reservoir towards a production well.

(20) At block **208**, fluid is produced from a production well. The fluid can include hydrocarbons, such as oil or gas, and aqueous fluids, such as the EOR fluid, brine from a water cut, and the like. At block **210**, the fluid is separated to form an aqueous stream and a hydrocarbon stream. The separation is generally performed in a water oil separation plant (WOSP), a water gas separation plant (WGSP), or a combined facility that separates both oil and gas from the entrained water.

(21) At block **212**, the hydrocarbon stream is sent to a facility for further processing. For example, the facility may be a refinery, a gas plant, and the like.

(22) At block **214**, the aqueous stream is recycled as a portion of the base fluid for forming the EOR fluid. If more base fluid is needed amount for making the EOR fluid, additional brine or fluid may be added, such as seawater, if proximate to the ocean. A further water hydrocarbon separation system may be used if needed to lower the amount of oil or gas entrained in the aqueous stream. The amount of surfactants in the aqueous stream can be tested, and additional surfactants added to bring the concentration up to the use concentration, for example, of about 0.2 wt. % at a ratio of 3/1 of the anionic-nonionic surfactant to the cationic surfactant.

#### Examples

(23) Surfactant solutions were prepared and placed at 25° C. and 95° C. for 1 day. The appearance of surfactant solutions in brines was observed visually to determine the compatibility. The compatibility results were recorded by the compatibility codes of A: clear solution: B: slightly hazy solution: C: hazy solution; and D: precipitation. IFT between surfactant solution and crude oil was measured by spinning drop tensiometer SDT (KRUSS) with video camera at different temperatures. The rotation speed used was 5000 rpm. Vonnegut formula was used to calculate IFT when the ratio of the drop length to the drop diameter was larger than 4.0, otherwise Laplace-

Young formula was used.

(24) The anionic surfactant used for the tests is sodium alkylphenol ethoxylate carboxylate (APEC). APEC was provided by Sinopec Shanghai Research Institute of Petroleum Technology with active content of 50 wt. %. The cationic surfactant is cetylpyridinium bromide (CPB). CPB is purchased from Sinopharm Chemical Reagent Co., Ltd with CP grade. The interfacial surface tension (IFT) is measured using a spinning drop tensiometer (SDT), equipped with a video camera from KRÜSS GmbH of Hamburg, Germany. The oil drop was injected into a glass tube filled with surfactant solution using a 10  $\mu$ L syringe. The tube containing surfactant solution and oil drop was placed in the instrument and accelerated to a constant rotation speed. The shape of oil drop was recorded to calculate IFT. The rotation speed mainly used was 5,000 rpm. Vonnegut formula was used to calculate IFT when the ratio of the drop length to the drop diameter was greater than 4.0, otherwise Laplace-Young formula was used. The data was automatically recorded by the software.

(25) Seawater was used for all tests. The seawater had a salinity of 57,670 ppm and a hardness of 2,760 ppm. As used herein, the hardness is generally a measurement of calcium and magnesium and does not include the counter ion. The compatibility of APEC in the seawater at 90° C. was poor. Two layers were observed and the solution became hazy after shaking. This indicates that the cloud point of APEC is not sufficient for use in a high temperature reservoir. However, mixing with CPB improved the compatibility, as shown by the solution becoming homogeneous and opalescence.

(26) Testing Surfactant Blend at Different Mixing Ratios

(27) FIG. 3 is a plot of the IFT of 0.2 wt. % APEC/CPB at 90° C. in seawater at different mixing ratios. As shown in FIG. 3, the IFT of a 0.2% APEC solution and seawater was 1.4 mN/m. The IFT of a 0.2% CPB solution in seawater is 0.2 mN/m. The IFT values of the 100% solutions of both APEC and CPB are too high for enhanced oil recovery.

(28) A lower IFT was obtained by mixing APEC with CPB. The IFT of the APEC/CPB mixtures decreased at first, and then increased with the mixing ratio. The lowest IFT of the APEC/CPB mixtures was  $4.0 \times 10^{-3}$  mN/m at a mixing ratio of about 3/1. This very low IFT value indicates good potential for improving oil recovery.

(29) The IFT of mixture was much lower than the IFT of the individual surfactants, due to the synergism between anionic-nonionic and cationic surfactants. Further, as noted above, the addition of the cationic surfactant to the solution of the anionic-nonionic surfactant improved the compatibility, as shown by a reduction in haze at 90° C.

(30) Testing Surfactant Mixtures at Different Salinities Over a Temperature Range

(31) FIG. 4 is a plot of the IFT of a 0.2% APEC/CPB mixture in the base fluid at a 3/1 ratio of APEC/CPB versus temperatures in brines with different salinities. The surfactant blends showed low oil/water IFT in brines with different salinities at different temperatures.

(32) The solution of 0.2% APEC/CPB maintained a low IFT of  $10^{-2}$  to  $10^{-3}$  mN/m in seawater (57,670 ppm) in a wide temperature range from 25 to 90° C., as shown in FIG. 2 and Table 2. At a temperature of 80° C., the IFT was  $10^{-3}$  mN/m. This indicates that this formulation could be used in reservoirs at high temperature.

(33) The surfactant mixtures have good compatibility, as shown in Table 1, and low IFT of  $10^{-2}$  to  $10^{-3}$  mN/m under different conditions with different salinities and temperatures, as shown in FIG. 4 and Table 2. The temperature range tested is from 25 to 90° C. and the salinity range is from 14420 ppm to 86505 ppm.

(34) TABLE-US-00001 TABLE 1 Compatibility of 0.2% APEC/CPB mixtures with different mixing ratios in seawater. m.sub.APEC/m.sub.CPB 0/1 1/3 1/1 2/1 3/1 4/1 1/0 25° C. A A A A A A A 95° C. A A A B B B C Note: A: clear solution; B: slightly hazy solution; C: hazy solution; and D: precipitation

(35) In addition to the favorable results in seawater, the 0.2% APEC/CPB solution maintained a low IFT of  $10^{-2}$  to  $10^{-3}$  mN/m in brines with a lower salinity of 14,400 ppm and also



higher salinity of 86,505 ppm in a wide temperature range from 25 to 90° C. (FIG. 2 and Table 2). These results indicate that this surfactant blend is tolerant of both temperature and salinity variations in reservoirs.

(36) TABLE-US-00002 TABLE 2 IFT data of 0.2% APEC/CPB = 3/1 in brines with different salinities at different temperatures. IFT/mN/m Temperature 0.25 × seawater seawater 1.5 × seawater (° C.) (14420 ppm) (57670 ppm) (86505 ppm) 25 0.054 0.067 0.044 40 0.045 0.060 0.037 60 0.019 0.032 0.011 80 1.2 × 10.<sup>sup.</sup>-3 6.8 × 10.<sup>sup.</sup>-3 5.9 × 10.<sup>sup.</sup>-3 90 2.4 × 10.<sup>sup.</sup>-3 4.0 × 10.<sup>sup.</sup>-3 8.4 × 10.<sup>sup.</sup>-3

#### Embodiments

(37) An embodiment described herein provides a method for enhanced oil recovery using a surfactant blend in an enhanced oil recovery (EOR) fluid. The method includes preparing the surfactant blend in a base fluid, by adding a first surfactant including a anionic-nonionic surfactant selected from sodium alkylphenol ethoxylate carboxylate (APEC), sodium alkyl ethoxylate carboxylate (AEC), sodium alkylphenol ethoxylate sulfate (APES), or sodium alkyl ethoxylate sulfate (AES), to the base fluid, and adding a second surfactant including a cationic surfactant including an alkyl pyridine salt to the base fluid forming the EOR fluid. The EOR fluid is injected into a reservoir through an injection well. Fluid is pushed to a production well. Fluid is produced from the production well, wherein the produced fluid includes hydrocarbons.

(38) In an aspect, combinable with any other aspect, the first surfactant includes APEC.

(39) In an aspect, combinable with any other aspect, the second surfactant includes cetylpyridinium bromide.

(40) In an aspect, combinable with any other aspect, the method includes forming a 0.2 weight percent mixture of the surfactants in the base fluid.

(41) In an aspect, combinable with any other aspect, the method includes adding the first surfactant to the base fluid in a 3:1 mass ratio to the second surfactant.

(42) In an aspect, combinable with any other aspect, the interfacial tension (IFT) of the EOR fluid is about 4.0×10.<sup>sup.</sup>-3 milliNewtons per meter (mN/m) at 90° C.

(43) In an aspect, combinable with any other aspect, the IFT of the EOR fluid is between about 10.<sup>sup.</sup>-2 and about 10.<sup>sup.</sup>-3 mN/m in a solution of about 58,000 ppm salinity had a temperature between about 25° C. and about 90° C.

(44) In an aspect, combinable with any other aspect, the IFT of the EOR fluid is about 10.<sup>sup.</sup>-3 at about 80° C.

(45) In an aspect, combinable with any other aspect, the method includes separating the produced fluid to form an aqueous stream and a hydrocarbon stream.

(46) In an aspect, combinable with any other aspect, the method includes sending the hydrocarbon stream to a facility.

(47) In an aspect, combinable with any other aspect, the method includes recycling the aqueous stream to form the EOR fluid.

(48) In an aspect, combinable with any other aspect, the method includes separating oil from the aqueous stream to form at least a portion of the base fluid.

(49) In an aspect, combinable with any other aspect, the method includes adding a makeup stream of base fluid to the aqueous stream.

(50) In an aspect, combinable with any other aspect, the method includes incorporating production chemicals into the EOR fluid, wherein the production chemicals include a biocide, a pH buffer, an acid, or a chelating agent, or any combinations thereof.

(51) In an aspect, combinable with any other aspect, the base fluid includes a brine.

(52) Another embodiment described herein provides an enhanced oil recovery (EOR) fluid. The EOR fluid includes a base fluid, an anionic-nonionic surfactant including one of sodium alkylphenol ethoxylate carboxylate (APEC), sodium alkyl ethoxylate carboxylate (AEC), sodium alkylphenol ethoxylate sulfate (APES), or sodium alkyl ethoxylate sulfate (AES), and a second

surfactant including a cationic surfactant including an alkyl pyridine salt.

(53) In an aspect, combinable with any other aspect, the first surfactant includes APEC.

(54) In an aspect, combinable with any other aspect, the second surfactant includes cetylpyridinium bromide.

(55) In an aspect, combinable with any other aspect, the EOR fluid includes a 0.2 weight percent mixture of the surfactants in the base fluid.

(56) In an aspect, combinable with any other aspect, the EOR fluid includes a 3:1 mass ratio of the first surfactant to the second surfactant.

(57) In an aspect, combinable with any other aspect, the interfacial tension (IFT) of the EOR fluid is about  $4.0 \times 10^{-3}$  millinewtons per meter (mN/m) at 90° C.

(58) In an aspect, combinable with any other aspect, the IFT of the EOR fluid is between about  $10^{-2}$  and about  $10^{-3}$  mN/m in a solution of about 58,000 ppm salinity at a temperature between about 25° C. and about 90° C.

(59) In an aspect, combinable with any other aspect, the IFT of the EOR fluid is about  $10^{-3}$  at about 80° C.

(60) Other implementations are also within the scope of the following claims.

## Claims

1. An enhanced oil recovery (EOR) fluid, comprising: a base fluid comprising a high salinity brine wherein the brine has a salinity in a range of about 14,000 ppm to about 87,000 ppm; a first surfactant comprising an anionic-nonionic surfactant selected from the group consisting of sodium alkylphenol ethoxylate carboxylate (APEC), sodium alkyl ethoxylate carboxylate (AEC), sodium alkylphenol ethoxylate sulfate (APES), and sodium alkyl ethoxylate sulfate (AES); and a second surfactant comprising a cationic surfactant comprising an alkyl pyridine salt; wherein the EOR fluid has a temperature between about 80° C. and about 90° C.; and wherein the base fluid comprises a 0.2 weight percent mixture of the first surfactant and the second surfactant in the base fluid.

2. The EOR fluid of claim 1, wherein the first surfactant comprises APEC.

3. The EOR fluid of claim 1, wherein the second surfactant comprises cetylpyridinium bromide.

4. The EOR fluid of claim 1, comprising a 3:1 mass ratio of the first surfactant to the second surfactant.

5. The EOR fluid of claim 4, wherein the interfacial tension (IFT) of the EOR fluid is about  $4.0 \times 10^{-3}$  millinewtons per meter (mN/m) at 90° C.

6. The EOR fluid of claim 4, wherein the IFT of the EOR fluid is between about  $10^{-2}$  to about  $10^{-3}$  mN/m in a solution of about 58,000 ppm salinity at a temperature between about 80° C. to about 90° C.

7. The EOR fluid of claim 4, wherein the IFT of the EOR fluid is about  $10^{-3}$  at about 80° C.

8. The EOR fluid of claim 1, wherein the brine has a hardness of about 50 ppm to about 5,000 ppm.

9. A method for enhanced oil recovery, comprising: preparing the EOR fluid of claim 1 by: adding the first surfactant to the base fluid; and adding the second surfactant to the base fluid forming the EOR fluid; injecting the EOR fluid into a reservoir through an injection well; pushing fluid to a production well; and producing fluid from the production well, wherein the produced fluid comprises hydrocarbons.

10. The method of claim 9, wherein the first surfactant comprises APEC.

11. The method of claim 9, wherein the second surfactant comprises cetylpyridinium bromide.

12. The method of claim 9, comprising adding the first surfactant to the base fluid in a 3:1 mass ratio to the second surfactant.

13. The method of claim 12, wherein the interfacial tension (IFT) of the EOR fluid is about  $4.0 \times 10^{-3}$  milliNewtons per meter (mN/m) at 90° C.

14. The method of claim 12, wherein the IFT of the EOR fluid is between about  $10^{-2}$  to about  $10^{-3}$  mN/m in a solution of about 58,000 ppm salinity at a temperature between about 80° C. to about 90° C.
  15. The method of claim 12, wherein the IFT of the EOR fluid is about  $10^{-3}$  at about 80° C.
  16. The method of claim 9, comprising separating the produced fluid to form an aqueous stream and a hydrocarbon stream.
  17. The method of claim 16, comprising sending the hydrocarbon stream to a facility.
  18. The method of claim 16, comprising recycling the aqueous stream to form the EOR fluid.
  19. The method of claim 18, comprising separating oil from the aqueous stream to form at least a portion of the base fluid.
  20. The method of claim 19, comprising adding a makeup stream of base fluid to the aqueous stream.
  21. The method of claim 9, comprising incorporating production chemicals into the EOR fluid, wherein the production chemicals comprise a biocide, a pH buffer, an acid, or a chelating agent, or any combinations thereof.
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