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(54) Title: METHOD OF USING A NON-ACIDIC STIMULATION FLUID IN HIGH TEMPERATURE SANDSTONE FORMA-
TIONS

(57) Abstract: A three step method of using a non-acidic stimulation fluid in high temperature sandstone formation is provided. The
method consists of using a preflush brine, sodium hydroxide solution, and an overflush brine.



PCT PATENT APPLICATION

**METHOD OF USING A NON-ACIDIC STIMULATION FLUID IN HIGH
TEMPERATURE SANDSTONE FORMATIONS**

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Field of the Invention

[0001] This **invention** relates to a method **for** using a **non-acidic composition** to stimulate an underground petroleum or hydrocarbon bearing formation. More specifically, the invention relates to a method of using a sodium hydroxide containing solution to stimulate a sandstone formation at high temperatures.

Background of the Invention

[0002] During **well** operations, chemicals are often injected into the underlying formation in a process known as stimulation. Stimulation of the formation is one technique that can be used to increase the net permeability of a formation or reservoir. Some exemplary known stimulation techniques include: **(1)** injection of chemicals into the wellbore to react with and dissolve conditions limiting production (e.g., the presence of clays and drilling solids); **(2)** injection of chemicals through the wellbore and into the formation to react with and dissolve portions of the formation, or to create alternative **flow** paths **for** recoverable hydrocarbons (e.g. acid-fracturing or **matrix-acidizing**); and **(3)** injection of chemicals through the wellbore and into the formation at pressures sufficient to cause fractures in the formation, thereby creating a flow channels through which hydrocarbons can more readily move from the formation into the wellbore.

[0003] In particular, sandstone formations are particularly susceptible to formation damage from formation minerals such as clay and other siliceous deposits. Historically, acid, or acid-based fluids have been used in the treatment or stimulation due to their ability to dissolve both formation minerals and contaminants (e.g., drilling fluid coating the wellbore or

that has penetrated into the formation) introduced into the wellbore/formation during drilling or remedial operations.

[0004] The removal of formation minerals and other deposits, such as clays or drilling solids, are key concerns in well completion operations. The known prior art techniques noted above typically involve highly concentrated acids, such as hydrofluoric acid (HF) and hydrochloric-hydrofluoric acid mixtures, which are both highly corrosive and can create dangerous operating conditions.

[0005] One difficulty encountered with traditional sandstone stimulation operations that employ HF is that HF can precipitate into the formation, causing formation damage and limiting matrix stimulation treatment efficiency. The damage caused by the fluoride precipitations are aggravated by higher temperatures. Another difficulty encountered with traditional HF sandstone stimulation is the acid reacts instantaneously with the formation, thereby limiting penetration of the acid into the formation. Therefore, it would be advantageous to use a stimulation fluid that does not form precipitants when it reacts with the sandstone formation at high temperatures and has a slower reaction rate.

Summary

[0006] The current invention provides a method for using a non-acidic stimulation fluid in high temperature sandstone formations. The non-acidic stimulation fluid is provided as an alternative to traditional stimulation methods that typically involve hydrofluoric and/or hydrochloric acids. The non-acidic stimulation fluid has a slower reaction time with the sandstone formation, thereby allowing for deeper penetration into the formation. Additionally, the non-acidic stimulation fluid does not form precipitations after reaction with the sandstone formation that can damage the wellbore upon further stimulation techniques.

[0007] In one embodiment, a method for stimulating a hydrocarbon containing formation using a non-acidic stimulation fluid is provided. The method includes involves three steps. In a first step, a preflush brine is injected into the sandstone formation. In the second step, a non-acidic stimulation fluid is injected into the foundation. Finally, in the third step, an overflush brine is injected into the sandstone formation. In this embodiment, no other stimulation fluid is used. The method is operable to allow efficient and effective penetration of the non-acidic stimulation fluid into the sandstone formation.

[0008] In one embodiment, the preflush brine is chosen from a group of halide-containing brines. In certain embodiments, the preflush brine can be aqueous ammonium chloride.

Preferred concentration of aqueous ammonium chloride is in a range of between 5 and 10% by weight, more preferably in a range of 5-8% by weight. In other embodiments, the preflush brine can be potassium chloride. In a preferred embodiment, concentration of potassium chloride will be in a range of between 3 and 8 % by weight, more preferably 4-6% by weight. In one embodiment, the preflush brine is injected into the sandstone formation first.

[0009] In one embodiment, the non-acidic stimulation fluid is a sodium hydroxide solution. In certain embodiments, the concentration of the sodium hydroxide solution is in a range of between 5 to 28% by weight. In one embodiment, the sodium hydroxide solution is injected into the sandstone formation after the preflush brine. In one embodiment, the non-acidic stimulation fluid is only sodium hydroxide solution. In this embodiment, no acid stimulation fluid is used. In another embodiment, the non-acidic stimulation fluid is a potassium hydroxide solution. In certain embodiments, the concentration of the potassium hydroxide solution is in a range of between 5 to 28% by weight. In certain embodiments, the potassium hydroxide solution is injected into the sandstone formation after the preflush brine.

[0010] In one embodiment, the overflush brine is selected from a group of halide-containing brines. In certain embodiments, the brine can be aqueous ammonium chloride in a concentration range between 5 to 10% by weight, alternatively between 5-7%, 7-9% or 9-10% by weight. In one embodiment, the overflush brine is injected into the sandstone formation third.

[0011] In certain embodiments, high temperatures are advantageous to increase the efficiency of the non-acidic stimulation fluid. In one embodiment, the non-acidic stimulation fluid is preheated in a range between 20°C to 70°C before injection. In certain embodiments, the non-acidic stimulation fluid is allowed to react with the sandstone formation for between 3 to 24 hours. In other embodiments, the temperature of the sandstone formation can be used to heat the non-acidic stimulation fluid after injection. In certain embodiments, the non-acidic stimulation fluid is allowed to react with the sandstone formation for between 3 and 24 hours.

Detailed Description of the Invention

[0012] Although the following detailed description contains many specific details for purposes of illustration, it is understood that one of ordinary skill in the art will appreciate that many examples, variations and alterations to the following details are all within the scope

and spirit of the invention. Accordingly, the exemplary embodiments of the invention described herein are set forth without any loss of generality, and without imposing limitations, relating to the claimed invention.

[0013] The present invention addresses problems associated with prior art methods for the stimulation of sandstone formations at high temperatures and the highly corrosive acids typically employed, and provides a new non-acidic stimulation methods. The methods described herein generally include a three step process consisting of injecting a preflush brine, followed by injecting a non-acidic stimulation fluid, and finally injecting an overflusli brine. Generally, the non-acidic stimulation fluid reacts with the sandstone formation slowly to enable deeper penetration into the sandstone formation. Additionally, the use of a non-acidic stimulation fluid does not result in the formation of precipitates during reaction.

[0014] As used herein, "sandstone" refers to any formation primarily composed of quartz sand and various forms of feldspar and clays. The grains of sandstone rock are traditionally sand-sized.

[0015] As used herein, "preflush" refers to a fluid pumped into the wellbore ahead of the main stimulation treatment fluids to displace potassium, sodium, and calcium ions in order to minimize the possibility adverse reactions with the treating fluids (e.g. clogging the pores of the foundation).

[0016] As used here, "overflush" refers to a fluid pumped into the wellbore after the stimulation treatment is complete. The overflusli fluid helps to push the main treatment fluid deeper into the sandstone formation and away from the near-wellbore formation to prevent precipitation of reaction products as the treatment fluids are flowed back.

[0017] As used herein, "brine" refers to an aqueous solution containing dissolved inorganic salts that is solid-free.

[0018] In one aspect, a method for injecting a non-acidic stimulation fluid into a high temperature sandstone formation is provided. In one embodiment, the method consists of three steps - injection a preflush brine solution, followed by injecting a non-acidic stimulation fluid, and then injecting an overflusli brine solution.

[0019] In one embodiment of this invention, the preflush brine solution can be selected from a group of halide-containing brines. In one embodiment, the preflush brine can be aqueous ammonium chloride in a concentration range of between 5 to 10% by weight, alternatively between 5-8% by weight. In other embodiments, the preflush brine can be

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[0023] Examples

[0024] The examples below are provided to show a certain exemplary non-acidic
sandstone stimulation fluid, as described herein, and its solubility in sandstone formation, at
differing concentrations and temperatures. A sodium hydroxide solution was allowed to react
with sandstone formation at varying temperatures and concentrations for three hours. As
shown in Table 1, a 5 % by weight sodium hydroxide solution, was p r e h e a t e d to temperatures

of 23°C and 49°C, and allowed to react with the sandstone formation for 3 hours. The solubility of the sodium hydroxide solution in the formation rock at these temperatures was 2.4 % by weight and 3.2% by weight, respectively. In another test, a 15% by weight sodium hydroxide solution, preheated to 70°C, was allowed to react with the sandstone formation and its solubility in the sandstone formation was 4.55% by weight. The examples show a clear correlation that increasing the temperature and concentration of the sodium hydroxide solution increases the sodium hydroxide solutions' permeability in the sandstone formation.

Table 1

<u>% wt concentration of NaOH</u>	<u>Reaction Temperature, °C</u>	<u>Sandstone solubility, %wt</u>
5% wt	23°C	2.4 % wt
5% wt	49°C	3.2 % wt
15% wt	70°C	4.55% wt

[0025] Although the present invention has been described in detail, it should be understood that various changes, substitutions, and alterations can be made hereupon without departing from the principle and scope of the invention. Accordingly, the scope of the present invention should be determined by the following claims and their appropriate legal equivalents.

[0026] The singular forms "a", "an" and "the" include plural referents, unless the context clearly dictates otherwise.

[0027] Optional or optionally means that the subsequently described *event* or circumstances may or may not occur. The description includes instances where the event or circumstance occurs and instances where it does not occur.

[0028] Ranges may be expressed herein as from one particular value, and/or to another particular value. When such a range is expressed, it is to be understood that another embodiment is from the one particular value and/or to the other particular value, along with all combinations within said range.

[0029] Throughout this application, where patents or publications are referenced, the disclosures of these references in their entireties are intended to be incorporated by reference

into this application, in order to more fully describe the state of the art to which the invention pertains, except when these reference contradict the statements made herein.

CLAIMS

That which is claimed is:

1. A non-acidic method for the stimulation of sandstone formations, the method comprising the steps of

 injecting a preflush brine solution into the wellbore such that the brine solution displaces potassium, sodium and calcium ions in the sandstone formation;

 injecting a basic solution into the wellbore; and

 injecting an overflush brine solution into the wellbore.
2. The method of claim 1 wherein the preflush brine is selected from a group of halide-containing brines.
3. The method of any of claims 1 and 2, wherein the preflush brine is aqueous ammonium chloride in a concentration range of between 5 to 10% by weight.
4. The method of any of claims 1-3, wherein the aqueous ammonium chloride brine of claim 3, wherein the concentration range is between 5-8% by weight.
5. The method of any of claims 1-4, wherein the aqueous ammonium chloride brine of claim 3, wherein the concentration range is between 8-9% by weight.
6. The method of any of claims 1-5, wherein the aqueous ammonium chloride brine of claim 3, wherein the concentration range is between 9-10% by weight.
7. The method of any of claims 1-6, wherein the basic solution is a sodium hydroxide solution.
8. The sodium hydroxide of claim 7, wherein the concentration of the sodium hydroxide solution is in a range of between 5 and 28 % by weight.
9. The sodium hydroxide of claim 7, wherein the concentration of the sodium hydroxide is in a range of between 5-8% by weight.
10. The sodium hydroxide of claim 7, wherein the concentration of the sodium hydroxide is in a range between 5-15% by weight.
11. The sodium hydroxide solution of claim 7, wherein the concentration of the sodium hydroxide is in a range between 20 to 70°C, prior to injection.

12. The method of any of claims 1-11, wherein the overflush brine is selected from a group of halide-containing brines.
13. The method of any of claims 1-11, wherein the overflush brine is aqueous ammonium chloride in a concentration range of between 5 to 10% by weight.
14. The aqueous ammonium chloride brine of claim 13, wherein the concentration range is between 5-7% by weight.
15. The aqueous ammonium chloride brine of claim 13, wherein the concentration range is between 7-9% by weight.
16. The aqueous ammonium chloride brine of claim 13, wherein the concentration range is between 9-10% by weight.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/071261

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/60 C09K8/72 C09K8/84
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

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.
A	US 2011/220360 AI (LINDVIG THOMAS [US] ET AL) 15 September 2011 (2011-09-15) paragraphs [0013] - [0016] the whole document -----	1-16
A	EP 0 654 582 AI (HALLIBURTON CO [US] HALLIBURTON ENERGY SERV INC [US]) 24 May 1995 (1995-05-24) page 3, lines 24-33 the whole document -----	1-16
A	US 2005/000694 AI (DALRYMPLE ELDON D [US] ET AL) 6 January 2005 (2005-01-06) example 3 -----	1-16
A	US 4 056 146 A (HALL BOBBY E) 1 November 1977 (1977-11-01) column 10, lines 7-21 the whole document -----	1-16



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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