US 20030150613A1

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2003/0150613 A1**

Freiter (43) **Pub. Date: Aug. 14, 2003**

(54) **ACIDIZING AND SCALE TREATMENT OF SUBTERRANEAN FORMATION**

(76) Inventor: **Edward R. Freiter**, Kingwood, TX (US)

Correspondence Address:
T.M. Breininger
ONDEO Nalco
ONDEO Nalco Center
Naperville, IL 60563-1198 (US)

(21) Appl. No.: **10/055,823**

(22) Filed: **Jan. 22, 2002**

Publication Classification

(51) **Int. Cl.**[7] **E21B 43/22**; E21B 43/27

(52) **U.S. Cl.** **166/279**; 166/307; 507/260; 507/274; 507/277

(57) **ABSTRACT**

A one step squeeze treatment of a subterranean formation involves the treatment with a treating solution comprising an acid, a scale inhibitor, and a reducing agent. The presence of the reducing agent prevents the iron ions in the system from reacting with and forming a precipitate with the scale inhibitor and maintains the iron ions in the ferrous state.

ACIDIZING AND SCALE TREATMENT OF SUBTERRANEAN FORMATION

FIELD OF INVENTION

[0001] This invention relates to the treatment of subterranean formations using acid and scale inhibitors. In a preferred aspect, the invention involves a one-step process for acidizing and scale treatment of a formation.

BACKGROUND OF THE INVENTION

[0002] The deposition of scale from both produced and source waters is common in oil-producing operations. Depositions occur downhole and in flow lines, separators, and other surface facilities. Scale is a problem in acid/scale squeeze operations where iron is present as an impurity either in the water or the reaction product of the acid with scale or oil field equipment. The reaction of the impure iron with scale inhibitors may produce solids that damage the formation or block production equipment. Because of the precipitation resulting from the mixing of the incompatible fluids, present procedures generally require two separate operations for wells that need both well work overs (e.g. acidizing) and scale squeezes. With two separate operations, the well is first treated with concentrated HCl, and the resulting spent acid is cleared out of the well. The second step consists of carrying out the squeeze operation with scale inhibitor. Another possibility is to treat the well sequentially by inserting pads of liquid between the HCl/spent acid and the fluids containing the scale inhibitor. These procedures are more expensive and result in more down time than a combined operation.

SUMMARY OF THE INVENTION

[0003] The method of the present invention involves the steps of

[0004] (a) injecting into a subterranean formation a treating solution of

[0005] (i) an acid that reacts with downhole materials and equipment to form $CaCl_2$, and iron ions,

[0006] (ii) a scale inhibitor, and

[0007] (iii) an additive capable of preventing the scale inhibitor from forming a precipitate with iron ions; and

[0008] (b) after a suitable shut in time, producing fluid from the well.

[0009] Each of the three fluid components of the treating solution may be as follows:

[0010] (1) Acid: Typical well treating acids include aqueous solution of 1 to 38% HCl, with 15% HCl being preferred. Other acids include sulfamic acid hydrofluoric acid, acetic acid, formic acid, etc. and mixtures thereof.

[0011] (2) Scale inhibitor: The preferred oil field scale inhibitors include phosphate esters, phosphonates, sulfonates, and polyacrylates. Other scale inhibitors include copolymers and terpolymers of acrylates, sulfonates and phosphonates, phosphinico polycarboxylic acids (PPCA) and mixtures thereof. Particularly useful scale inhibitors include 2-hydroxyethyl imino bis methylene phosphonic acid, fatty amine phosphonates, triethanolamine phosphate ester, DETA phosphonate (pentaphosphonates) and TETA phosphonate (hexaphosphonates).

[0012] (3) The additive for preventing or inhibiting the formation of a precipitate of iron ions and the scale inhibitor may take a variety of forms such as chelating agents, or agents for maintaining the iron ions in the ferrous state. The preferred additive, however, is a reducing agent for reducing Fe^{+++} to Fe^{++}. Example reducing agents include ascorbic acid, citric acid and thioglycolic acid, oxalic acid, and erythorbic acid and mixtures thereof. The preferred reducing agent is erythorbic acid.

[0013] The three water soluble or dispersible components may be used in one solution, or pumped in any sequence. It is preferred that they be used in one treating solution in the following concentrations (wt. %):

	Range	Preferred Range	Most Preferred Range
HCl	1–38	10–15	15
Scale Inhibitor	0.5–50	0.5–10	1–5
Additive (e.g. reducing agent)	0.05–50	0.1–5	0.1–1.0

[0014] Operation

[0015] In the oil field squeeze operation, the treating fluid may be premixed ("batched") or mixed continuously ("on the fly") during injection. All of the components may be blended together or they may be injected in any sequence of 1, 2 and 3.

[0016] (1) injection of a solution HCl

[0017] (2) addition of reducing agent

[0018] (2) injection of the scale inhibitor solution.

[0019] In either process, the precipitate preventative (e.g. reducing agent) reacts with the iron ions so that upon contact with the scale inhibitor, no precipitate is formed.

[0020] The amount of treating fluid squeezed into the formation will depend on several factors including the degree of scaling, the type of scale, length of perforations, etc. From 1 to 100 barrels per foot of perforations will be satisfactory for most treatments.

[0021] The squeeze operation may be carried out with other work over procedures and may be in accordance with procedures well known in the art, including the use of corrosion inhibitors and other well treating chemicals.

[0022] Once the well is returned to production chemicals squeezed into the formation will slowly be produced along with well fluids and will treat the well.

EXAMPLES

[0023] Bottle tests carried out at 180° F. to determine the compatibility of HCl or solutions and scaling agents with and without the precipitate preventative (e.g. reducing agent).

[0024] The following aqueous solutions were prepared:

Sample	Ingredients
A	15% HCl
B	15% HCl + 3,000 ppm Fe^{+3}
C	spent 15% HCl + 22 wt. % $CaCl_2$
D	spent 15% HCl + 22 wt. % $CaCl_2$ + 3000 ppm Fe^{+3}

[0025] Tests were run by adding 0.6 wt. % erythorbic acid (reducing agent) to Samples B, C, and D, followed by the addition of 3.5 wt. % of a scale inhibitor. The samples were observed for a precipitate. Comparison tests were run on Samples B, C, D without the addition of the erythorbic acid. Table I presents the results.

[0026] The tests on Sample D demonstrate the effectiveness of the presence of the reducing agent with the first 5 scale inhibitors tested.

TABLE I

Sample	A		B		C		D
Scale Inhibitor	No EA	With EA	Without EA	With EA	Without EA	With EA	Without EA
2-hydroxyethyl imino bis methylene phosphonic acid	Not run	OK	OK	Not run	OK	OK	Cloudy/ppt
Fatty Amine phosphonate	Not run	Cloudy/ppt (1)	OK	Not run	OK	OK	Cloudy/ppt (2)
triethanolamine phosphate ester	Not run	OK	OK	Not run	OK (4)	OK	Cloudy/ppt
DETA phosphonate (pentaphosphonate)	Not run	Cloudy/ppt (1)	Cloudy/ppt	Not run	OK (3)	OK (?)	Coundy/ppt
BMHT phosphonate	Not run	OK	Cloudy/ppt	Not run	OK	Cloudy/ppt (1)	Cloudy/ppt
EDA phosphonate	OK	Cloudy/ppt (1)	Cloudy/ppt	Not run	Cloudy/ppt	Cloudy/ppt	Cloudy/ppt
polyvinylsulfonate	Not run	Not run	OK	Not run	OK	Not run	OK
polyacrylic acid	OK	OK	OK	Cloudy/ppt (5)	Cloudy/ppt	Not run	Not run

EA = Erythorbic Acid
1 = starts cloudy -> slight ppt starts after 1 hour, clear at 180° F.
2 = slightly cloudy
? = slightly cloudy -> clears
3 = immediate ppt goes into solution on soaking
4 = formed gel on heating
5 = small amount of ppt on heating
6 = ppt formed soon after starting, did not go back into solution at 180° F.

What is claimed is

1. In a method of treating a subterranean formation with a treating solution containing acid and iron ions, the improvement wherein the treating solution further contains

(a) a scale inhibitor, and

(b) an additive capable of preventing or inhibiting the iron ions from forming a precipitate with the scale inhibitor:

2. The method of claim 1 wherein the iron ions enter the treating solution by the acid reacting with downhole equipment or materials.

3. The method of claim 1 wherein the acid is HCl.

4. The method of claim 3 wherein the additive is a reducing agent for reducing the iron ions to the ferrous state.

5. The method of claim 4 wherein the reducing agent is erythorbic acid.

6. The method of claim 4 wherein the scale inhibitor is selected from the group consisting of phosphonates, phosphate esters, polyacrylates, sulfonates, copolymers and terpolymers of acrylates, sulfonates and phosphonates, phosphinico polycarboxylic acid.

7. A method of treating a subterranean formation comprising the steps of

(a) mixing an aqueous solution of

(i) HCl,

(ii) a scale inhibitor, and

(iii) an additive for preventing or inhibiting the scale inhibitor from forming a precipitate with any iron ions in the water,

(b) injecting the treating solution into the formation whereby the reaction of the HCl with downhole equipment or materials forms iron ions and whereby the presence of an effective amount of the additive (iii) inhibits the iron ions from reacting with and forming a precipitate with the scale inhibitor.

8. The method of claim 7 wherein the HCl is present in a concentration of 1 to 38%.

9. The method of claim 7 wherein the scale inhibitor is selected from the group consisting of phosphonates, phosphate esters, and polyacrylic acid.

10. The method of claim 7 wherein the scale inhibitor is selected from the group consisting of phosphonates, phosphate esters, polyacrylates, sulfonates, copolymers and terpolymers of acrylates, sulfonates and phosphonates, phosphinico polycarboxylic acid, phosphoric acid and salts thereof and is present in the treating solution at a concentration of between 0.5 and 50 wt. %.

11. The method of claim 7 wherein the additive is a reducing agent and is present in the treating solution at a concentration of between 0.05 and 30 wt. %.

12. The method of claim 11 wherein the reducing agent is selected from the group consisting of erythorbic acid, ascorbic acid, citric acid, thioglycolic acid, oxalic acid and mixtures thereof.

13. An aqueous solution for treating a subterranean formation which comprises:

(a) From 5 to 28 wt. % HCl,

(b) From 0.5 to 10 wt. % of a scale inhibitor, and

(c) From 0.05 to 5 wt. % of a reducing agent for maintaining any iron in the treating solution in the ferrous state.

14. The treating solution of claim 13 wherein the scale inhibitor consisting of phosphonates, phosphate esters, polyacrylates, sulfonates, copolymers and terpolymers of acrylates, sulfonates and phosphonates, phosphinico polycarboxylic acid.

15. The treating solution of claim 13 wherein the reducing agent is erythorbic acid.

* * * * *