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(54) Title: OIL GEL

(57) Abrégé/Abstract:
A fracturing fluid for use in fracturing subterranean formations comprises a hydrocarbon base. Neutralized alkyl phosphate esters are complexed with metallic cations, to form a gel, in the hydrocarbon base.

A B S T R A C T

A fracturing fluid for use in fracturing subterranean formations comprises a hydrocarbon base. Neutralized alkyl phosphate esters are complexed with metallic cations, to form a gel, in the hydrocarbon base.

OIL GEL

Field of the Invention

The present invention relates to methods and compositions for fracturing subterranean formations. In particular, the present invention provides a novel fracturing fluid for fracturing such formations.

Background of the Invention

In order to increase the productivity of oil and gas wells, or to bring back into production wells that have essentially gone dry, it is common practice to conduct a procedure known as fracturing the well. In such a procedure, fluids known as fracturing fluids, are injected into the well at very high hydrostatic pressures. The fluids are typically viscous gels, and act under pressure to open pores and cracks in the formation, thereby to increase the overall permeability of the well. Typically, the fluids also are used to transport proppants, such as sand or ground walnut shells into the cracks and pores, thereby to ensure that the pores and cracks formed during fracturing remain open under the lower pressures that will exist after fracturing, when the well is producing.

The fluid that has been used to fracture the formation is removed by the introduction of viscosity lowering agents into same, which permit the fluid to be more easily pumped from the

formation. These agents are known as breakers because they tend to break down the fracturing gel. Breakers can act on a gel in a number of ways, such as by the random oxidation of polymers to shorten the chain length thereof. In the present invention, a breaker is utilized to adjust the pH of a gel, to break same by hydrolysis.

The fracturing fluid of the present invention is a phosphate alkyl ester gel. It is known that a gel can be produced by mixing trivalent cations, such as aluminum, with a phosphate alkyl ester. However, gels obtained with known phosphate alkyl esters have not been commercially acceptable, because the viscosity developed with same has been insufficient or slow to develop. Moreover, to obtain such gels, tank mixing has been needed.

Phosphate alkyl esters may be mono-esters, di-esters or tri-esters. In the mono-ester, one primary mono-hydric alcohol, of C_5-C_{16} length is ester linked to a phosphate. A di-ester has two such alkyl alcohols linked to a phosphate. A tri-ester has three alkyl alcohols linked to it. The applicants have discovered that commercially valuable gels are feasible with a di-ester content above 50%, preferably above 65%, and a tri-ester content below 5%. The remainder may be mono-ester.

The applicants enhance gel development in two important ways. First, the phosphal alkyl esters are neutralized with primary amines. Secondly, the applicants utilize a surfactant to enhance gel development. An appropriate surfactant is ammonium alkyl (C_6-C_{20}) sulfate.

In order to break the gel of the present invention the preferred breaker is a pH adjusting breaker, such as calcium oxide and sodium carbonate. It is preferred that the breaker be encapsulated in a porous inert substance, such as nylon.

In a broad aspect, then, the present invention relates to a fracturing fluid for use in fracturing subterranean formations comprising: a hydrocarbon base; and neutralized alkyl phosphate esters complexed with metallic cations, to form a gel, in said hydrocarbon base.

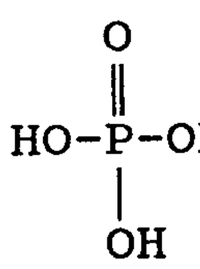
Brief Description of the Drawings

In drawings that illustrate the present invention by way of example:

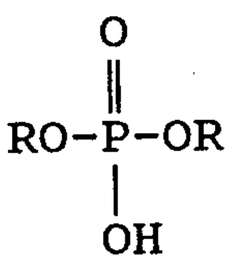
Figure 1 is a graph illustrating the effect of pH and surfactant on the phosphate alkyl ester gels of the present invention.

Detailed Description

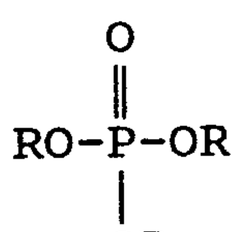
The phosphate ester gels of the present invention are made from primary mono-hydric alcohols of C_5-C_{16} chain length. It is preferred to utilize alcohols of chain length C_8-C_{12}, but it will be understood that since the gels of the present invention are intended to act on hydrocarbon fluids, such as diesel fuel, kerosene, or other common hydrocarbon fluids, the selection of an optimal chain length alcohol will be a matter of choice for one skilled in the art. The alkyl alcohols are combined with phosphates, by known techniques to produce mono-di and tri-alkyl esters which may generally be represented as follows:



mono-alkyl phosphate ester



di-alkyl phosphate ester



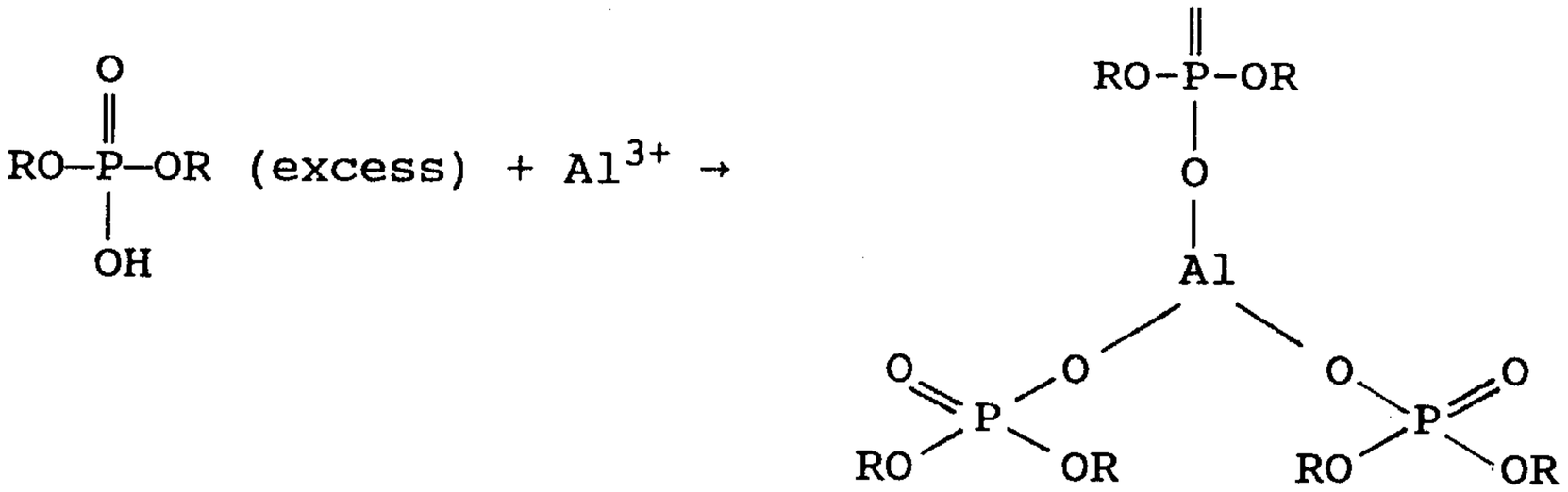
tri-alkyl phosphate ester

The relative proportions of mono-alkyl, di-alkyl and tri-alkyl esters are important. The applicant has discovered that the di-alkyl phosphate ester content must be at least 50% for any gel development to occur, and must be at least 65% for commercially feasible gel to form. Moreover, tri-alkyl phosphate ester content must be lower than 5%, or poor gel rheological characteristics will result. There must be at least a small percentage of mono-alkyl phosphate ester present to initiate gelling.

Primary amines are used to neutralize esters. The quantity of amine used will, of course depend on the amine. However, a suitable amine is mono-ethanol amine (MEA). From 1% to 5% of a concentrated (99%) MEA solution (relative to the weight of the phosphate alkyl esters) is used to produce a desired level of neutralization (pH) in the esters. A preferred pH is about 1.4-1.8.

The partially neutralized phosphate ester is then mixed in the hydrocarbon fluid to be gelled, with a trivalent cation, either aluminum or ferric. It is, moreover, preferred to utilize chelated ions, since these readily disperse in organic solvents, thereby enhancing the rate of gelation. Examples of suitable compounds are aluminum isopropoxide, aluminum sec-butoxide, oxy-aluminum octoate, and so on.

The phosphate-alkyl esters and cations form a mesh-like network in the hydrocarbon fluid, resulting in a gel. The hypothesized reaction is as follows:



It will be understood that such a network will transform the essentially two dimensional phosphate-alkyl ester to a three dimensional, very viscous gel.

The gelling rate can moreover be greatly enhanced using a surfactant. Sulphates or sulphonate groups provide the necessary alteration of surface chemistry to result in enhancement of reaction rates. Aluminum alkyl (C_6-C_{20}) sulfate has been found to be an appropriate surfactant.

The effects of partial neutralization and the use of surfactants are illustrated in Figure 1. In the examples shown in Figure 1, it can be seen that the lowest viscosity is achieved with an unneutralized gel, and no surfactant. It will be understood that in each case 8 litres per cubic metre diesel

oil, of a 70% dialkyl phosphate ester are utilized, with 8l/cubic metre of aluminum tri-isopropoxide.

In the example neutralized to a pH of 1.57, resulting viscosity is about doubled, with the use of a surfactant resulting in a further tripling of the achieved viscosity. As shown, if the pH is permitted to rise, viscosity will be lowered somewhat. This information can be utilized, however, to advantage, to design gels with viscosity characteristics to particularly match those desired for fracturing a given formation.

To form a gel in a hydrocarbon solvent according to the present invention, 0.5 - 1.5% (by weight of hydrocarbon) partially neutralized phosphate alkyl ester are utilized with 0.025 - 0.2% surfactant and 0.1 - 1.5% trivalent cation. About 80% of the maximum gel viscosity is attained, typically, in the first minute of mixing. The constituents can and advantageously are, therefore, blended "on the fly" as they are pumped into a formation.

The gel may be broken by the use of pH adjusting breakers, such as soda ash, caustic, lime, amines, and acids.

It will be appreciated, therefore, that the present invention provides a reliable viscous gel for use with

hydrocarbon solvents, which can be broken on a consistent and effective basis.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A fracturing fluid for use in fracturing subterranean formations comprising:

(a) a hydrocarbon base;

(b) neutralized alkyl phosphate esters complexed with

(c) metallic cations, to form a gel, in said hydrocarbon base.

2. A fracturing fluid as claimed in claim 1, wherein said alkyl phosphate esters include mono-alkyl phosphate ester, di-alkyl phosphate esters and tri-alkyl phosphate esters.

3. A fracturing fluid as claimed in claim 2, wherein at least 50% of said alkyl phosphate esters are di-alkyl phosphate esters.

4. A fracturing fluid as claimed in claim 2, wherein at least 65% of said alkyl phosphate esters are di-alkyl phosphate esters.

5. A fracturing fluid as claimed in claim 4, wherein no more than 5% of said alkyl phosphate esters are tri-alkyl phosphate esters.

6. A fracturing fluid as claimed in claim 5, wherein the alkyl component of said alkyl phosphate esters are formed from primary monohydric alkyl alcohols of chain length C_5-C_{16}.

7. A fracturing fluid as claimed in claim 5, wherein the alkyl component of said alkyl phosphate esters are formed from primary monohydric alkyl alcohols of chain length C_8-C_{12}.

8. A fracturing fluid as claimed in any one of claims 1 to 7 wherein said alkyl phosphate esters are neutralized with a primary amine.

9. A fracturing fluid as claimed in claim 8, wherein said alkyl phosphate esters are neutralized to a pH of about 1.4 to 1.8.

10. A fracturing fluid as claimed in claim 8 or 9, wherein said alkyl phosphate esters are neutralized with mono-ethanol amine (MEA).

11. A fracturing fluid as claimed in any one of claims 1 to 10 wherein said metal cation is a trivalent ion.

12. A fracturing fluid as claimed in claim 11, wherein said metal cation is a trivalent aluminum ion.

13. A fracturing fluid as claimed in claim 12, wherein the source of said metal cation is selected from the group including aluminum isopropoxide, aluminum sec-butoxide, oxy-aluminum octoate and other chelated aluminum compounds.

14. A fracturing fluid as claimed in any one of claims 1 to 13 further including a surfactant.

15. A fracturing fluid as claimed in claim 14, wherein said surfactant is selected from the group including sulphates and sulfonates.

16. A fracturing fluid as claimed in claim 14 wherein said surfactant is ammonium alkyl (C_6-C_{20}) sulfate.

17. A fracturing fluid as claimed in claim 14, including 0.5 - 1.5% of said alkyl phosphate ester, 0.025 - 0.2% of said surfactant and 0.1 - 1.5% of said metal cation.

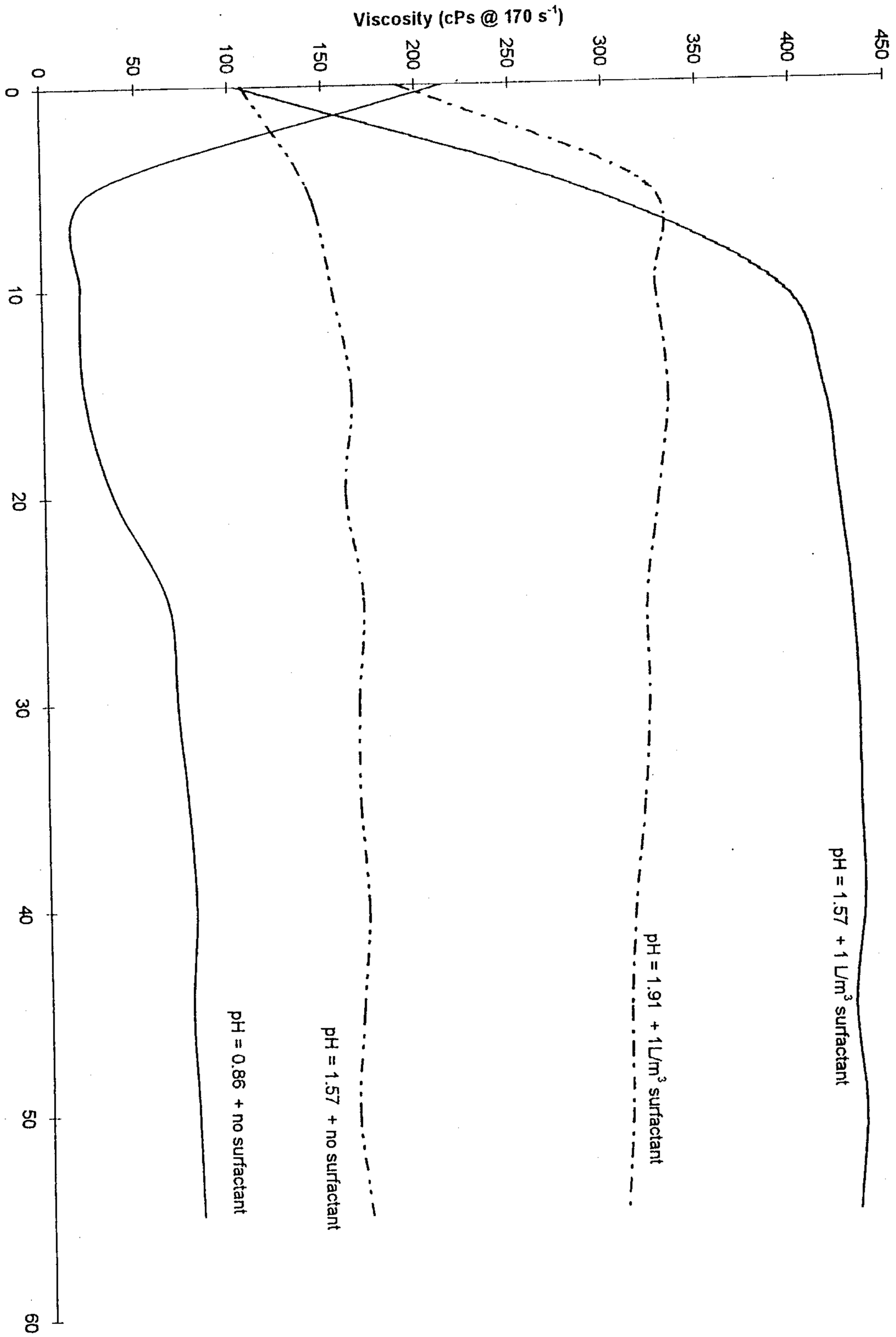

On The Fly System @ 80°C
using 8L/m3 gel. and 8L/m3 act.
Viscosity (cPs @ 170 s-1)
0
50
100
150
200
250
300
350
400
450
0
10
20
30
40
50
60
Time (min)
pH = 1.57 + 1 L/m3 surfactant
pH = 1.91 + 1L/m3 surfactant
pH = 1.57 + no surfactant
pH = 0.86 + no surfactant

FIGURE 1