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AQUEOUS FOAMS FOR GEOTHERMAL DRILLING FLUIDS I. SURFACTANT SCREENING*

Peter B. Rand

Sandia Laboratories, Albuquerque, New Mexico 87185**

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Aqueous foam is a promising drilling fluid for geothermal wells because it will not harm the producing formation and would eliminate the errosion problems of air drilling. Successful use of aqueous foam will require a high foaming surfactant which will: 1. Be chemically stable in the harsh thermal and chemical environment, and 2. form stable foams at high temperatures and pressures. This paper presents the procedures developed to generate and test aqueous foams and the effects of a 260°C temperature cycle on aqueous surfactant solutions. More than fifty selected surfactants were evaluated, with representatives from the amphoteric, anionic, cationic, and nonionic classes included. Most surfactants were severely degraded by this temperature cycle; however, some showed excellent retention of their properties. The most promising surfactant types were the alkyl and alkyl aryl sulfonates and the ethoxylated nonionics.

INTRODUCTION

Aqueous foam is a promising drilling fluid for the underpressured hard rock formations frequently found in geothermal reservoirs. Its primary advantages are: 1. It should not harm producing formations, 2. It allows high drilling rates, and 3. Low annular velocities will eliminate the errosion problems of air drilling. Successful use of aqueous foam for geothermal drilling will require a surfactant system which will have sufficient chemical stability to withstand the harsh thermal and chemical environment found in geothermal wells. In addition to chemical stability, it must also be capable of forming stable foams at high temperatures and pressures. Some work has been done with aqueous foam in high temperature environments by Union Oil[1] for geothermal drilling and for steam stimulation by Chevron USA.[2] A recently completed study by Maurer Engineering for the Department of Energy[3] discusses the problems and promise of aqueous foams for use as geothermal drilling fluids.

Because of its low density, successful use of foam will require a high pressure rotary drilling head suitable for geothermal well use. This will allow balanced drilling thus allowing control of formation water and steam. Corrosion problems may require the use of nitrogen rather than air to make the foam. If corrosion inhibitors can be found that will work in the high temperature geothermal environment, this may not be necessary.

The first step in developing foam drilling fluids for geothermal use is to find chemically stable foaming agents or surfactants to make the foam. This paper will present the results of a study to determine the thermal stability of a wide variety of commercially available surfactants in aqueous solution. Tests were run on the solution and foams made with the solution before and after exposure to 260°C for two hours. These tests have shown that several types of commercially available surfactants may be suitable foaming agents for geothermal drilling.

EXPERIMENTAL

Aqueous solutions of the surfactants were exposed to the following temperature cycle: a. ambient to 260°C-2.0 hours, b. 260°C-2.0 hours, c. 260°C-ambient-3.0 hours. The solutions were contained in heavy wall stainless steel tubing with "Swagelok" end caps. The solutions were prepared by mixing fifty percent by weight of the surfactant as received in deionized water. A few surfactants were aged as either 1.0 or 0.2 weight percent solutions in a Baroid 500 cc high temperature aging cell due to limited solubility. This is noted where applicable in the data.

Aqueous foams for evaluation were made by metering nitrogen gas and the surfactant solution into a static mixer. This system provided uniform small celled foams with controlled density. Density and drainage time to fifty percent by volume were measured on foams made with surfactants that had and had not been exposed to the high temperature cycle. The solution pH was also measured before and after exposure. The foams were also evaluated qualitatively by observing their cell structure. Ratings of good, fair, and poor were assigned on the basis of the nonuniformity of their cell structure. The density of all foams was controlled to 45.0 ± 5.0 Kg/m^3 except as noted.

SURFACTANTS

A wide variety of high foaming surfactants were selected for evaluation on the basis of their chemical structure and/or supplier's recommendations. Amphoteric, anionic, cationic, and nonionic types with varying chemical structure were evaluated. The books by Schwartz and Perry[4,5] and

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McCutcheons[6] were used extensively to determine chemical structure and availability respectively.

Amphoteric surfactants evaluated were the betaines, amido betaines, sulfo amido betaines, an imidazolene compound, and a propriatary fluorochemical material. Most anionic surfactants evaluated were sulfonic acid salts or sulfonates. Alkyl, alkyl aryl, and perfluoro alkyl sulfonates were included. Other anionic types tested were an ethoxylated alkyl sulfate and an amide linked carboxylic acid salt. Cationic types evaluated were an imidazolene compound, ethoxylated tertiary amines, and a proprietary fluorochemical material. The nonionic surfactants tested were ethoxylated fatty alcohols, alkyl aryl alcohols, and a polyoxypropylene - polyoxyethylene block copolymer.

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RESULTS AND DISCUSSION

The data presented in Tables I - III on the effect of a 260°C temperature cycle on various surfactants was selected from data on more than fifty surfactants. The data includes all surfactants that showed promise and representative data on all types tested. The surfactants are identified by chemical type whenever possible and are subdivided into amphoteric, anionic, cationic, nonionic and propriatary classes.

The density given was obtained on the foam dispensed for the original drainage tests. A few of the poorer foaming surfactants would not make foams of 45.0 ± 5.0 Kg/m^3 in our generator. This is noted in the original cell structure column. The density of 45.0 ± 5.0 Kg/m^3 was chosen as representative of the preformed stable foams used as drilling fluids. This density is equivalent to a liquid volume fraction of 0.045 or a weight of 0.37 LBS/GAL.

Foam drainage is defined as the time to fifty percent weight loss of a preformed foam. It is a measure of density stability of the foam. Foams with long drainage times or good density stability are desirable for drilling fluid applications. The drainage data is presented as the time in minutes to 50 percent by weight drainage and the percentage difference in drainage time between the original and exposed sample.

All foams tested were qualitatively evaluated for cell structure and given ratings of good--small uniform cells, fair-nonuniform cell structure and poor-nonuniform cells with large voids. This test is important because it indicates that degradation products from the surfactant are acting as antifoamers or defoamers in the solution. This implies that higher temperatures or longer times would give solutions incapable of making foams. This would be disasterous for foam drilling fluid applications. Some foams made with surfactants exposed to 260°C retained or even improved their drainage time; however, they would not make fine-uniform celled foams indicating the importance of this rating. Many surfactant solutions would not make foams after exposure to 260°C. This is noted with a "no foam" rating in the aged cell structure column.

The last column in the tables gives the change in pH of the aqueous solution before and after exposure to 260°C. Without knowing the degradation mechanisms of the surfactant evaluated, the reason for a change in pH is difficult to determine. For this series of tests, pH was treated as a relative value indicative only of some change in the solution.

The data are presented somewhat arbitrarily in the order of decreasing drainage time after exposure to 260°C. Although drainage time is important, the true value of a surfactant for geothermal foam drilling must also consider the change in drainage, in foam cell structure, in pH and in many other factors yet to be evaluated. This ordering system does tend to put the best surfactants at the top of the list in each class. All data presented are the average of three determinations.

The aging data presented in Table I on amphoteric surfactants shows that these materials, as a class, performed poorly. Only one, a coco betaine, had good cell structure after aging accompanied by a 28.0 percent decrease in drainage time. A cetyl betaine gave a small decrease in drainage time; however, the poor foam cell structure after aging indicates problems will arise after longer exposure times. Most of the amphoteric surfactants produced no foam at all after exposure to 260°C. It is interesting to note that one of the surfactants giving no foam is another coco betaine, indicating that there are differences between surfactants sold as the same chemical type from different manufacturers. One surprise in these data was the failure of a fluorochemical surfactant, normally noted for its chemical stability.

The anionic surfactants showed less degradation as a class as shown in Table II. All anionic surfactants evaluated made foam after our 260°C cycle. The best anionic surfactants evaluated were a sodium alkyl aryl polyether sulfonate and a sodium alkyl amide sulfonate which both show small changes in drainage time, good cell structure after exposure, and small changes in pH. The first surfactant listed, a sodium alkyl ester sulfonate, showed a large increase in drainage time. In this case, hydrolytic cleavage of the ester linkage will generate a fatty alcohol which is an excellent foam stabilizer which probably explains this surprising result. Although promising, this result must be viewed with caution as the foam cell structure was rated only fair after exposure to 260°C. Other anionic surfactants which will be evaluated in future tests are the alpha olefin sulfonate and the triethanol amine alkyl aryl sulfonate. Because of the known hydrolytic instability of the sulfuric esters (sulfates), very few were evaluated. Data on an ethyoxylated ammonium alkyl sulfate is given.

Data on cationic, nonionic, and proprietary surfactants are given in Table III. The cationic

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surfactants, as a class, performed poorly. One, an ethoxylated amine, had an increase in drainage time; however, it had poor cell structure after aging. Conversely, the nonionics, as a class, performed well. After exposure to 260°C, two showed an increase in drainage time and made foams with good cell structures. One, an ethoxylated fatty alcohol, gave very little shift in solution pH. Several proprietary foaming agents, recommended for foam drilling, were evaluated. One system, which is recommended for use as a foaming agent with steam in oil well stimulation procedures, performed well. This system gave a moderate decrease in drainage, good cell structure, and a small change in solution pH after aging.

These data, on the effect of a 260°C temperature cycle on surfactant solutions, represent the first step in finding useful surfactants for geothermal foam drilling. Promising surfactants from these tests will now be exposed to acidic, basic, and simulated geothermal brine solutions at 260°C and higher temperatures. These tests will establish the chemical stability of surfactant solutions in various chemical environments. The final step to establish surfactant usefulness will be to make and evaluate aqueous foams at high temperatures and pressures in an autoclave. Successful surfactants from these tests will then be formulated with additives such as corrosion inhibitors, scale inhibitors, antioxidants, and caustic chemicals to make foaming agent systems for geothermal drilling.

CONCLUSIONS

Techniques have been developed to expose aqueous surfactant solutions to a high temperature cycle, to generate foams with controlled density, and to evaluate the foams made. These techniques were used to evaluate more than fifty surfactants to establish their resistance to a 260°C temperature cycle as a first step in finding surfactants for use as foaming agents for geothermal drilling. Most surfactants evaluated were severely degraded by the 260°C temperature; however, about one in five showed good resistance. These promising surfactants will be tested after exposure to various chemical environments at 260°C and higher temperatures in a continuing program to find foaming agents for geothermal drilling.

ACKNOWLEDGEMENTS

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TABLE I: EFFECT OF 260°C ON SELECTED AMPHOTERIC SURFACTANT SOLUTIONS

Chemical Type	Density (Kg/m^3)	Time (Min) to 50% Drainage Original	Aged	Delta % Drainage	Cell Structure Orig.	Aged	Delta pH
Cetyl Betaine	46.4	5.63	5.40	-4.10	Good	Poor	+1.45
Coco Betaine	45.6	6.83	4.90	-28.3	Good	Good	+1.82
Coco Amido Betaine	47.0	5.66	3.48	-38.5	Good	Poor	+1.62
Coco Betaine	44.6	6.79	No Foam	——	Good	No Foam	+1.83
Sulfo Coco Amido Betaine	45.3	5.33	No Foam	——	Good	No Foam	+0.67
Potassium Coco Amino Acid Salt	44.5	4.85	No Foam	——	Good	No Foam	-1.89
Coco Imidazoline Betaine	45.7	6.82	No Foam	——	Good	No Foam	-1.72
Proprietary Fluorochemical	44.4	9.83	No Foam	——	Good	No	-1.27

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TABLE II: EFFECT OF 260°C ON SELECTED ANIONIC SURFACTANT SOLUTIONS

Chemical Type	Density (Kg/m^3)	Time (Min) to 50% Drainage Original	Aged	Delta % Drainage	Cell Structure Orig.	Aged	Delta pH
Sodium Alkyl Ester Sulfonate	41.4	7.28	24.2	+232.	Good	Fair	-2.65
Sodium Alpha Olefin Sulfonate	43.8	7.84	7.38	-12.0	Good	Good	-2.73
Triethanol Amine Alkyl Aryl Sulfonate	45.1	8.74	6.95	-20.4	Good	Fair	-0.28
Sodium Alkyl Aryl Polyether Sulfonate	46.1	5.12	4.94	-3.51	Good	Good	+0.78
Sodium Alkyl Amide Carboxy Acid Salt	46.4	5.36	4.72	-19.4	Good	Fair	+1.41
Sodium Alkyl Amide Sulfonate	43.1	4.97	4.54	-8.60	Good	Good	-0.32
Sodium Alkyl Sulfonate	44.7	5.62	4.21	-25.0	Good	Poor	-1.21
Potassium Perfluoro Alkyl[1] Sulfonate	92.8	2.58	3.85	+49.2	High Density	Fair	-0.76
Ethoxylated Ammonium Alkyl Sulfate	44.5	5.88	1.55	-73.7	Good	Poor	-3.88

NOTES: 1. Aged and tested as 0.2%/wt. solution.

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TABLE III: EFFECT OF 260°C ON SELECTED CATIONIC, NONIONIC, AND PROPRIETARY SURFACTANT SOLUTIONS

Chemical Type	Density (Kg/m^3)	Time (Min) to 50% Drainage Original	Aged	Delta % Drainage	Cell Structure Orig.	Aged	Delta pH
CATIONIC							
Ethoxylated Coco Amini	43.1	3.17	3.90	+23.0	Good	Poor	-0.96
Propriatary Fluorochemical	46.7	8.06	No Foam	——	Good	No Foam	-2.07
Coco Hydroxyethyl Inidazoline	54.7	4.73	No Foam	——	High Density	No Foam	No Data
NONIONIC							
Alkyl Aryl Ethoxylated Alcohol	47.2	3.87	4.32	+11.6	Good	Good	-1.70
Polyoxyethylene-Polyoxypropylene Block Copolymer	57.4	4.94	4.13	-16.4	High Density	Fair	-2.65
Ethoxylated Fatty Alcohol	44.7	3.42	4.11	+20.2	Good	Good	-0.02
PROPRIETARY							
None Given	43.8	8.63	7.16	-17.0	Good	Good	+0.23
None Given	45.3	6.92	3.46	-50.0	Good	Poor	+0.30

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