AMERICAN ASSOCIATION of DRILLING ENGINEERS

2009 NATIONAL TECHNICAL CONFERENCE & EXHIBITION, NEW ORLEANS, LOUISIANA

AADE XXX (Leave Blank – Paper number to be assigned): The Development of an Effective Water-Wetting Cement Spacer for the Displacement of Non-Aqueous Fluids (NAF)

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ABSTRACT

During the course of drilling operations, cement is extensively used for the purpose of sealing the annulus after the casing string has been run, sealing a zone where substantial drilling fluid losses are occurring, used to set a kickoff plug, or plug for abandonment of the well. Critical to any cementing operation is the development of a compatible spacer that separates the cement from any non-aqueous fluid (NAF) during displacement while simultaneously water-wetting the casing and formation for optimal bonding. Typically, several chemical spacers can be used in the course of the displacement of NAF to cement. The inability to effectively displace the NAF and water-wet the casing and the rock formation can lead to excessive non-productive time, costly squeeze jobs, the inability to pressure up the well, casing failures, and communication between zones.

This work presents our design and testing in the development of a new cement pre-flush spacer. The observations and results from the laboratory testing clearly indicate that this spacer technology effectively cleans and would water-wet the casing and formation during the displacement.

INTRODUCTION

Fundamental to the success of oilfield cementing, is the ability to effectively alter the condition of a surface to water-wet [1, 2]. This is difficult to consistently achieve when drilling with non-aqueous fluids that can differ significantly in chemical composition and properties, as required to achieve drilling performance. However, failure to completely displace a NAF from the wellbore and water-wet the casing and formation prior to cementing can be costly [3].

Typically, a series of aqueous or water continuous spacers are used to displace the NAF from the wellbore. These spacers may contain viscosifiers, weighting material, surfactants, solvents, mutual solvents, and/or mixtures thereof [4]. Factors such as temperature, salinity, hardness, pH, solids content, oil-water ratio, and oil type can all simultaneously influence the performance and the ultimate success of these chemical additives.

As the fluids are pumped they commingle creating a mixed interface of spacer and NAF. The use of inappropriate types and concentrations of these chemical additives can lead to fluid incompatibilities that can be detrimental if they are incorrectly matched to the conditions to which they are to be exposed in the wellbore. This can result in phase separation, settling of solids, poor cleaning, insufficient water-wetting, and spikes in viscosity, to name a few. Significant fluctuations in viscosity that can be formed at the interface of a NAF and an aqueous spacer can lead to channeling, which could be further exacerbated in a non-concentric wellbore [5-8].

A cement pre-flush spacer was designed to effectively displace a NAF from the wellbore while reversing the wettability of the casing and formation from oil-wet to water-wet. Displacement technology that incorporates the NAF by a solubilization process has proven effective in the laboratory and field [9]. A comprehensive study to understand the chemical interactions between NAF and pre-flush spacer at various spacer/NAF ratios was undertaken. The observations and results will focus on the fundamental interactions occurring at the NAF/spacer interface and the corresponding relationship upon cleaning, wettability, and compatibility.

Cement Pre-Flush Spacer Development

Integral to the successful development of the cement pre-flush spacer is the proper design of the chemical additives. Selection of the surfactant was based upon extensive phase behavior studies in complex systems of water/brine, oil, surfactant, and co-surfactant. The phase behavior of any surfactant or surfactant blend, hence the ability to clean and water-wet, are significantly influenced by temperature, salinity, oil/water ratio, and other factors. A systematic study was conducted to evaluate and design a robust system based on a fundamental understanding of the chemical interactions and the behaviors at a set of conditions. The system was selected that exhibited the highest propensity for solubilization of oil in the aqueous phase, at concentrations of 5 and 10 vol% of surfactant.

The representative chemical components that make up the remainder of the cement pre-flush spacer are listed in **Table 1**.

Table 1. Additives of Cement Pre-Flush Spacer

Cement Pre-Flush Spacer
Water or low salinity brine
Polymer
Mesophase additive
Barite

To evaluate the spacer, a series of laboratory scale experiments that simulated a set of displacement conditions were conducted. The tests were performed to assess the ability of the cement pre-flush spacer to water-wet and clean the casing and formation at the spacer/NAF interface. The drilling fluids tested included NAF formulated with various base oils, such as olefin, paraffin, enhanced mineral oil, and diesel. The interface was evaluated over a broad range of temperatures, e.g. 40 °F, 150 °F, and 250 °F. The laboratory experiments evaluated the interfacial tension, the capacity of the pre-flush spacer to water-wet and clean the casing and formation, rheological compatibility at the spacer/NAF interface, the phase inversion from oil to water continuous using surfactant screening conductivity test (SSCT), and microscopy studies to understand the mechanism involved in the phase inversion. The results demonstrate the capacity of the mesophase cement pre-flush spacer to effectively water-wet and clean at the spacer/NAF interface.

Results and Discussion

Interfacial Tension (IFT)

The interfacial tension is a measure of the attractive forces between two liquids, in this case water and oil. The reduction of tension between water and oil is integral in optimizing an aqueous surfactant solution to maximize its cleaning and water wetting efficiency. Ultimately, any reduction in the surface tension between the two phases will be dictated by the addition of a surfactant(s) under a set of conditions. Selection of the proper surface active agent(s) or surfactants that can reduce the IFT between the aqueous and organic phases will play a significant role in the overall effectiveness and ability of any cement spacer system to water-wet, clean, and to perform in a prescribed environment. **Figure 1** illustrates the dynamic interfacial tension measured when only water and synthetic base oil are in contact at 150 °F, 16-17 mN/m.

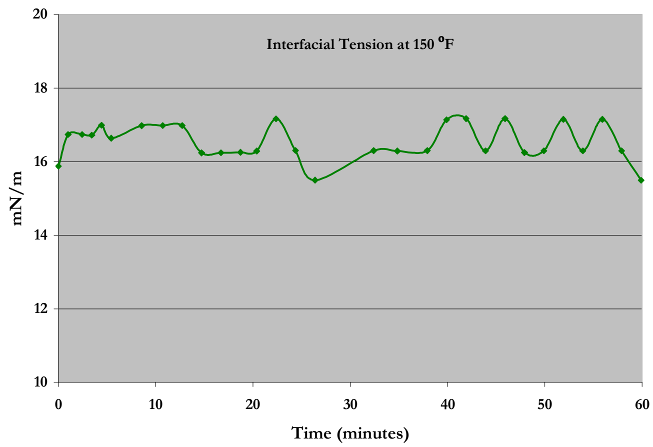

Figure 1. Interfacial tension measurements of water/brine in contact with synthetic base oil (olefin).

A surfactant can lower the interfacial tension between an aqueous and organic phase; however, the magnitude is completely dependent upon the type and amount of surfactant(s) added and the conditions to which they are exposed. By comparison, the mesophase surfactant solution that was developed for this cement pre-flush spacer exhibited the ability to further promote a significant reduction in IFT, reducing the interfacial tension between water and the synthetic base oil by approximately two orders of magnitude at 150 °F, see **Figure 2**.

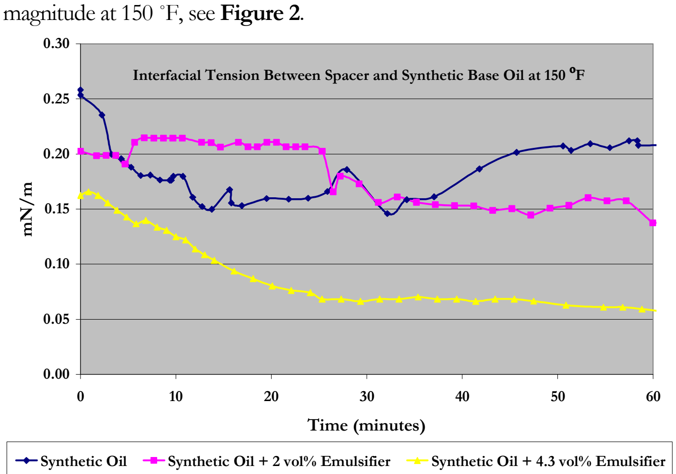

Figure 2. Interfacial tension measurements of the aqueous mesophase surfactant solution with synthetic base oil.

Vial Tests

Vial tests were used in the initial screening to determine the effective concentration of mesophase additive and to evaluate the cleaning capacity of the cement pre-flush spacer. A series of vial tests that simulated the spacer/NAF interface at ratios of 90/10, 75/25, and 50/50 were prepared to quickly test the ultimate effectiveness of the surfactant package concentration and its temperature stability.

After dynamic mixing, the vials were allowed to static age at temperatures of, 40 °F, 150 °F, and 250 °F, for 16 hours. Afterwards, the vials were re-mixed and the contents poured out. A light rinsing with water to remove any water wet solids revealed the cleaning and water wetting efficacy of the spacer with NAF contamination. The cleanliness of the vials in **Figure 3** are an indication of the spacer/synthetic NAF ratio that the mesophase cement pre-flush spacer can invert the oil continuous synthetic NAF to a water continuous fluid based upon temperature. Even at very high levels of synthetic NAF contamination, the spacer performs exceptionally well based upon visual cleanliness of the vials below. Qualitatively, based upon the visual trend in **Figure 3**, the vial test indicates the ability of the pre-flush spacer to water-wet at the spacer/synthetic NAF interface, performing better at higher temperatures in the order 250 °F (best) > 150 °F > 40 °F.

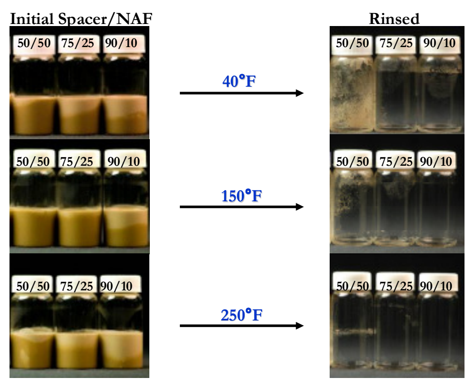

Figure 3. Evaluation of the temperature dependence of a 14 ppg cement pre-flush spacer with 14 ppg NAF.

The performance of any surfactant(s) is not only influenced by temperature, but also a host of variables, including changes in the composition of the base oil or other components that comprise a NAF. Ultimately, a pre-flush was developed that is tolerant of significant changes in temperature, see **Figure 3,** and composition that typically affect overall performance of surface active agents. **Figure 4** illustrates, in a simple vial test, the effects of changes in base oil type and composition. The results shown in **Figure 4** were performed at 250 °F with a 14 ppg cement pre-flush spacer and NAF commonly used for drilling. Clearly, this cement pre-flush performs exceptionally well on synthetic NAF even at high NAF contamination. In this case, at 250 °F, the pre-flush spacer exhibits a performance trend of synthetic (best) > diesel > mineral oil.

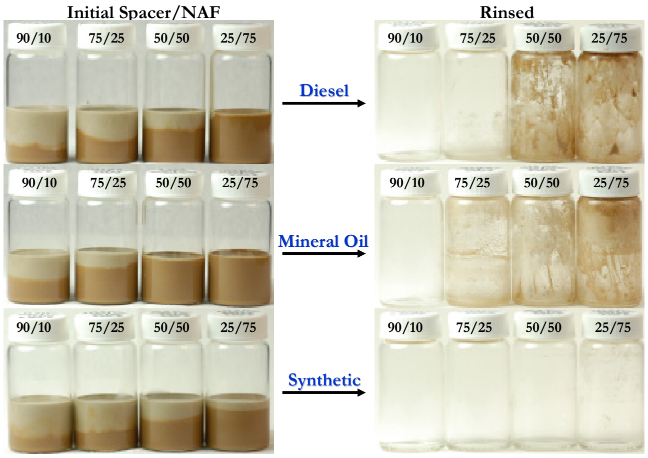

Figure 4. Effectiveness of the cement pre-flush spacer with three types of base oils at 250 ˚F.

Beaker Tests

A beaker test was performed to simulate the water wetting ability of the spacer under low-shear conditions. Using a pre-weighed beaker, the NAF was applied to the inside of the beaker and re-weighed. Pre-heated spacer was then added to the beaker, and the beaker was placed into a pre-heated thermal cup. The fluid was mixed at 100 rpm for 10 minutes on a Fann 35 to simulate shear rate and contact time. Afterwards, the cement pre-flush was poured out and the beaker was lightly rinsed with water to remove any remaining water continuous fluid and water-wet solids. The beaker was dried and re-weighed. Visual inspection provided an indication of the spacer's effectiveness. **Figure 5** shows the results of the beaker test with 14 ppg NAF. The results indicate greater than 99% of NAF removal when in contact with 100% cement pre-flush spacer at 150 ˚F.

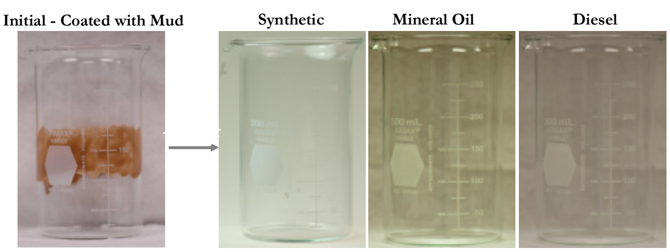

Figure 5. Beaker tests conducted at 150 ˚F with 100% cement pre-flush spacer.

Similar beaker tests were conducted to examine the performance of the cement spacer when contaminated with NAF. **Figure 6** shows the results of the beaker test when the pre-flush is contaminated with 25 vol% of 14 ppg NAF. The severely NAF-contaminated spacer still performs exceptionally well with synthetic drilling fluid. It cleaned 100% of the drilling fluid placed into the original beaker. Everything was completely water-wet. Despite the other beaker's appearance in **Figure 6**, the spacer contaminated with 25 vol% mineral oil NAF and 25 vol% diesel NAF removed 93% and 86%, respectively, of the drilling fluid added to the beaker.

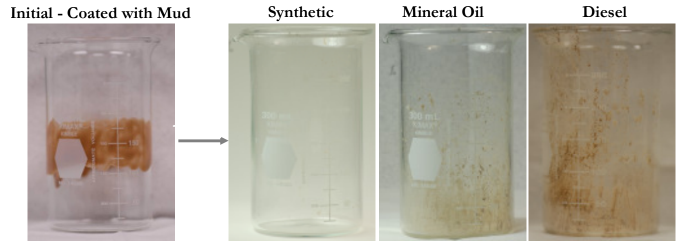

Figure 6. Beaker test conducted at 150 ˚F with cement pre-flush spacer contaminated with 25 vol% 14 ppg NAF.

Fluid Compatibility: Rheology of Cement Pre-Flush Spacer/Non-Aqueous Fluid

The compatibility of the cement pre-flush spacer and NAF is important for successful displacement of the oil-based drilling fluid. The difficulty in displacing NAF to a weighted and viscosified water-based fluid is the increase in viscosity created by a thick emulsion at the interface between the two fluids. Several spacer/NAF mixtures were prepared and their rheology measured at 40 ˚F and 150 ˚F. **Table 2** lists the rheological properties measured on a Fann 35 of a cement pre-flush spacer, a synthetic NAF, and several spacer/NAF ratios. The results show no appreciable increases in viscosity over the spacer/NAF ratios tested. The rheology can be adjusted by the addition or omission of additional viscosifier. The rheologies in **Table 2** reveal the compatibility of the spacer/synthetic NAF and the lack of spikes in the rheological profile of the interface.

Table 1. Rheology of 14 ppg cement pre-flush spacer/14ppg synthetic NAF and blends at 40 ºF and 150 ºF.

SBM, %	0	10	25	50	75	90	100
spacer, %	100	90	75	50	25	10	0
	Rheology at 40 ºF						
100 rpm, cP	34	36	43	38	73	64	86
6 rpm, cP	18	19	18	14	17	15	24
3 rpm, cP	17	17	15	11	14	13	20
PV, cP	29	31	43	36	122	102	100
YP., lb/100 ft^2	28	29	33	33	45	41	70
	Rheology at 150 ºF						
100 rpm, cP	25	34	33	28	30	30	28
6 rpm, cP	17	18	20	14	12	10	10
3 rpm, cP	15	16	19	12	12	9	9
PV, cP	4	12	11	11	38	36	34
YP., lb/100 ft^2	26	32	31	28	22	20	20

Surfactant Screening Conductivity Test (SSCT)

The SSCT measures the phase inversion from oil to water continuous by monitoring relative changes in conductivity [10]. The test is relatively straightforward in what is essentially a very basic titration. As the fluid phase inverts from oil continuous to water continuous, the device measures the electrical activity of the fluid and the meter displays the the "apparent" wettability in dimensionless units called Hogans (Hn). In the paper referenced by Heathman *et al* , give detailed operating procedures for calibrating and performing the test. The spacer is mixed while being heated to the stable test temperature and a relative conductivity base line is established, in this case 150 °F and 125 Hn. After establishing the relative base line conductivity with the spacer at the test temperature, it is poured out and the blender cup cleaned. Then pre-heated NAF is added and mixed. The conductivity should read 0 Hn. Once the NAF reaches the testing temperature, pre-heated spacer is titrated in 10 cc increments and the conductivity is recorded. The titration of cement spacer is continued until reaching the phase inversion and a stable relative conductivity is achieved Upon completion, the spacer/NAF mixture is poured out and the cup rinsed, see **Figure 7**. The cleanliness of the blender cup serves as a good qualitative measure of the ability of the spacer contaminated with NAF to water-wet a steel surface. **Figure 8** demonstrates results from the tests with the mesophase cement pre-flush spacer and 10, 12.5, and 14 ppg synthetic NAF at 150 °F.

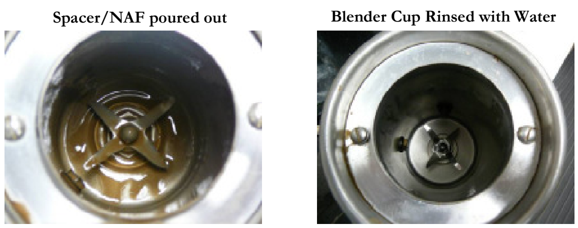

Figure 7. Blender cup upon completion of the SSCT and after rinse with water. Note that after rinsing the blender cup is clean without residual NAF.

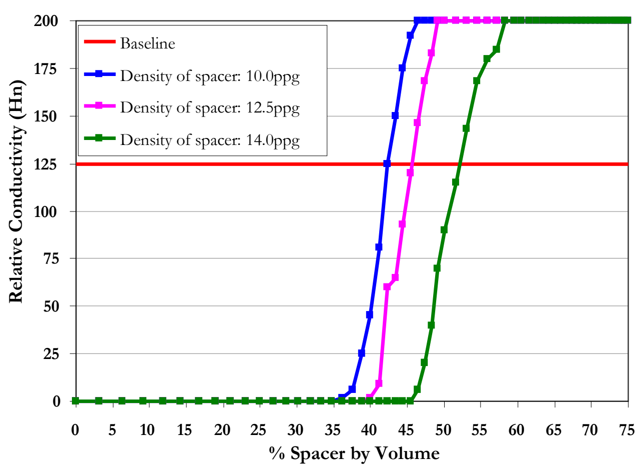

Figure 8. SSCT relative conductivity of the cement pre-flush spacer with synthetic NAF at 10, 12.5, and 14 ppg.

To further understand the results from the SSCT and to confirm the phase inversion from an oil continuous fluid to a water continuous fluid a solids-free spacer and NAF were prepared, see **Figure 9**. By examining certain ratios of the spacer/NAF, the phase inversion can be confirmed by fluorescence microscopy. Green oil-soluble dye was added to the solids-free NAF to trace whether the oil is in the external phase of the solution or within the internal phase of a droplet. **Figure 10** confirms the phase inversion of the fluids from oil continuous to water continuous.

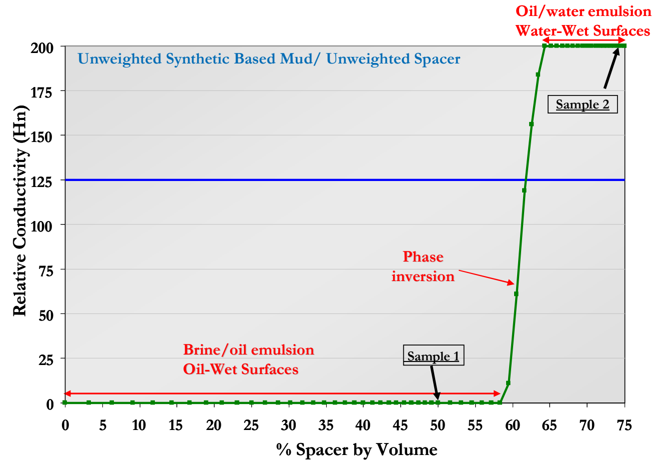

Figure 9. Corresponding spacer/NAF ratios where sampling for fluorescence microscopy occurred.

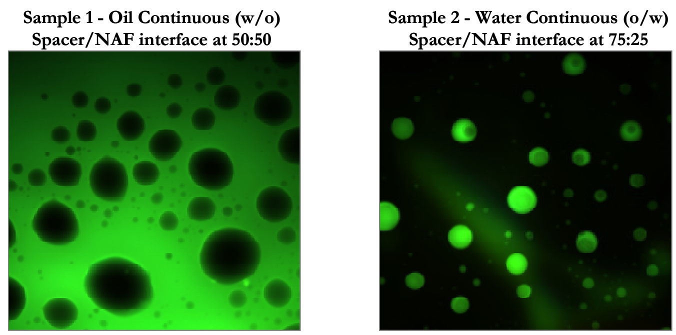

Figure 10. The fluorescence microscopy of Sample 1 (50:50 ratio) and Sample 2 (75:25 ratio) from the SSCT with solids-free fluids.

CONCLUSIONS

- A mesophase cement pre-flush spacer was developed to displace, water-wet and clean the casing and formation prior to cementing.
- The results prove that the cement pre-flush spacer has the ability to phase invert an NAF from oil continuous to water continuous.
- The mesophase additive used to formulate the cement pre-flush spacer is not sensitive to changes in temperature up to 250 °F, changes in type of base oil, or changes in NAF formulation.
- The cement pre-flush spacer can water-wet even with high NAF contamination, especially with synthetic NAF.

ACKNOWLEDGEMENTS

The authors thank the management of Baker Hughes for allowing us to publish the results. Thanks to Anuradee Witthayapanyanon, Qusai Darugar and Venkata Palla.

NOMENCLATURE

NAF	=	*non-aqueous fluid*
mN/m	=	*milli-Newtons per meter*
PV	=	*plastic viscosity*
YP	=	*yield point*
cP	=	*centipoise*
Lb/bbl	=	*pounds per barrel*
Lb/gal	=	*pounds per gallon*
ppg	=	*pounds per gallon*
Lb/100 ft²	=	*pounds per 100 square feet*
°F	=	*temperature in Fahrenheit*
SSCT	=	*Surfactant Screening Conductivity Test*
Hn	=	*Hogans*

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