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# Novel Free-Flowing Powdered Surfactant Composites Designed for Cement Spacer Applications

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## Abstract

Traditional liquid oilfield chemicals used to remove oil-based muds and alter the wettability of the formation from oil-wet to water-wet are becoming obsolete. With the growing demand for new environmentally friendly cement spacer systems, future conventional cement spacer mixing and pumping processes using liquid materials will be dominated by on-the-fly processes that use cement units and low-foaming powdered materials to enhance borehole cleaning before cementing operations. Powdered chemicals are suitable for oilfield applications because they can reduce capital and operating costs and can simplify the logistics of transporting bulk chemicals to well sites.

This paper presents the chemical design of newly developed novel free-flowing powdered surfactant composites comprising surface-functionalized mesoporous vehicles and surfactant blends, and it discusses the use of these composites in cement spacer applications. The surfaces of these vehicles have been modified to optimize host-guest interactions and densify non-Newtonian fluids. The controlled release of the adsorbed surfactant blends from the powdered surfactant composites into the treating fluid is discussed in detail. Furthermore, extensive mud removal tests are performed to examine the efficiency and potential of these powdered spacer blends for removing oil-based muds at different temperatures.

## Introduction

Oil-based muds (OBMs) are usually used in the rotary drilling process of subterranean formations. In this process, the drilling mud lubricates the drill bit, carries cuttings from under the drill bit and transports them to the surface. The drilling mud provides sufficient hydrostatic pressure within the well to prevent the wellbore from collapsing as a result of the forces experienced underground.

The formation of a filter cake on the surface of a subterranean formation prevents the filtration of formation

fluids into the wellbore and loss of drilling mud in the formation. There are three methods of forming filter cakes: (i) using bridging particles and polymeric additives, (ii) filtering the drilling mud into the subterranean formation during the drilling operation and (iii) injecting a fluid loss additive as a spot treatment into the region of the well experiencing fluid loss during the completion operation. OBMs often contain oil wetting agents to alter the wettability of the weighting agent and the drill solids from a water-wet state to an oil-wet state. Therefore, the filter cake typically adheres strongly to the wall of the subterranean formation.

This filter cake, however, could hamper the subsequent cementing of the casing. The presence of this oil-wet filter cake can prevent the adherence of aqueous cement slurries to the walls of the formation due to the incompatibility between the aqueous cement slurries and the organic contamination. Therefore, removing the oil-wet filter cake, residual oil and all traces of the drilling mud as well as changing the wettability of the wall of the subterranean formation from an oil-wet state to a water-wet state before the cementing operation are essential to ensure a good bond between the cement slurry, casing and wall of the subterranean formation.

To remove the filter cakes and fluid loss pills before the cementing operation, oil-based pre-flushes containing an oil-based fluid, a surfactant and a solvent/mutual solvent are often used to break the oily outer layer of the invert mud and remove the organic phase (Crook et al. 2008; Newhall 2006, Soucy et al. 2019). Subsequently, a water-based spacer is pumped into the well to clean the wellbore, alter the wettability of the formation from the oil-wet state to the water-wet state and avoid the contamination of the aqueous cement slurry with an oil-based pre-flush.

The cement spacer which should be prepared from its constituent materials at the wellsite, typically comprises water, a gelling agent, weighting solids, fluid loss materials, a pH buffer and a surfactant package. These constituent materials

are often added individually into the mixer and the mixing time is about 4–6 hours depending on the hydration time of the gelling agent and the efficiency of the batch mixer to achieve a uniform blend. The spacer must then be tested to ensure that it is within an appropriate density range for the wellbore. However, the use of batch mixers may be problematic because the volume of the spacer is restricted by the capacity of the batch mixers.

Consequently, the water-based spacer is prepared, stored at a blending facility and then transported to the wellsite. Independent of the particular chemistry of the water-based spacer, the maximum storage time of the finished spacer before pumping into the wellbore is about 12 hours due to the gravitational settling of the weighting solids. Furthermore, the surfactant package must be added into the spacer at a low shear rate to prevent excessive foaming, which extends the operating time and increases operating costs.

To reduce the capital and operating costs associated with the preparation of the cement spacer, the on-the-fly mix process was developed using cement units for mixing and pumping the water-based cement spacer simultaneously (Li et al. 2016). This process uses very high shear rates for a short period to combine the constituent materials into a single homogeneous fluid with specific properties. This fluid is then pumped into the wellbore immediately after mixing. However, mixing the surfactant package with the water-based spacer at very high shear rates often results in excessive foaming and thus, a large amount of defoamer is required. Furthermore, the short mixing time of this process may negatively affect the hydration of the gelling agent. The insufficient hydration of the gelling agent often reduces the viscosity of the water-based spacer and promotes the gravitational settling of the weighting agent.

Therefore, there is a clear need in the industry to overcome some of the problems associated with cleaning oil-based muds, and preparing the water-based cement spacer for on-the-fly applications.

The primary objective of the present study is to provide novel powdered surfactant structures that readily resolve the aforementioned problems. A secondary objective is to provide a powdered cement spacer blend (cement spacer in a bag) suitable for blending on the fly.

### **Design of the powdered surfactant structures**

The powdered surfactant structures for cement spacer applications comprise surfactant blends adsorbed onto novel surfactant sorption structures. These powdered surfactant structures include liquid chemical additives adsorbed onto a porous solid material, wherein the internal and external surfaces of the porous solid material are covered with a

surface-functionalizing moiety. When the resulting powdered surfactant structure is combined with a treatment fluid, the liquid additives are slowly released from the structure into the treatment fluid, which is then introduced into the wellbore.

In summary, the powdered surfactant structure comprises a surfactant sorption structure with the following three components:

- (i) A first component comprising a high surface area (HSA) solid support that includes a plurality of pores in the HSA solid support. The inside surface of the pores and external surface of the HSA structure comprise hydroxyl groups used as points to bond to the second and third components.
- (ii) A second component comprising a nitrogen-containing branched or linear polymer; and
- (iii) A third component comprising a branched or linear polyol.

The second and third components of the surfactant sorption structure are linked to each other to form an adduct, which is then covalently bonded to or adsorbed on the first component.

Alternatively, the second and third components can become adsorbed on the inside surface of the pore via the hydrogen bonds between these components and the oxygen of the hydroxyl group on the inside surface of the pore.

The surfactant sorption structures used in the present study differ from typical solid supports, as they are reactive adducts of nitrogen- and polyol- containing compounds and solids. The surfactant sorption structure comprises a porous solid support that provides structural integrity to reactive adducts, with all active groups, which are readily accessible to the surfactant blends, located inside the pores and pore channels of the porous solid substrates.

Modifying the surface chemistry of the solid support included in the surfactant sorption structures enhances its surfactant adsorption capacity. Nevertheless, under the conditions described herein, this delays the desorption process of the chemical additives from the powdered surfactant structures, thereby providing thermal stability and long-term fluidity to the treatment fluid at elevated temperatures. This improvement in the chemical delivery capabilities of the surfactant sorption structures results in controlling the concentration of the desorbed chemical additives in the treatment fluid while mixing the powdered surfactant structure with the treatment fluid on-the-fly.

The desorption rate of the surfactant blend from this novel powdered surfactant structure is pH-dependent. The powdered surfactant structure is designed to allow the desorption rate of the surfactant blend to first proceed slowly during a controlled initiation phase and then hastily during a rapid phase. The controlled initiation phase transitions to the rapid phase when

the pH of the treatment fluid reaches at least 9. The desorption rate is also intrinsically regulated by the pH of the treatment fluid, which may be below 9 initially, and preferably in the range of pH 6 to pH 8. As the surfactant blend is desorbed during the controlled initiation phase, the relative concentration of the basic groups on the surfactant sorption structure increases, gradually raising the pH of the treatment fluid, which then accelerates the desorption rate of the surfactant blend. The length of the controlled initiation phase may be controlled by varying the concentration of the basic groups on the HSA structure. This controlled initiation phase provides the time to mix the powdered surfactant structure with the treatment fluid on the fly and place the treatment fluid in a desired depth in the formation without excessive foaming.

### Manufacturing the surfactant sorption structure

As mentioned above, the second and third components of the surfactant sorption structure were linked to each other to form a pre-prepared composite that could be adsorbed on the first component.

The pre-prepared composite was synthesized via a reflux route of a solution containing a nitrogen-containing compound, a polyol and glacial acetic acid for 5 hours at 70°C. The active pre-prepared composite was then extracted.

Mesoporous silica support (SBA-15) was freshly synthesized similarly to a previously reported procedure ( Zhao et al. 1988). SBA-15 was then impregnated with a solution of the pre-prepared active composite using the incipient wetness process. The surfactant sorption structure was finally dried at 105°C for 5 hours.

### Effect of pH on the adsorption of an ethoxylated surfactant onto the surfactant sorption structure

To determine the effect of pH on the adsorption capacity on the newly developed surfactant sorption structure, three samples of the newly developed surfactant sorption structure containing 10 wt%, 20 wt%, and 30 wt% of the pre-prepared composite were used. The high concentrations of the pre-prepared composite were purposefully selected to evaluate their adsorption capacity. Approximately 0.2g of each sample was mixed with 150 ml of an aqueous solution containing 100 mg/L of an ethoxylated surfactant. The pH of the initial solution was from pH 4 to 12 using NaOH (0.1M) and HCl (0.1M). The slurry was mixed at room temperature at a low shear rate for 4 hours. The surfactant sorption structure was filtered using 0.45 µm HPLC filter with a disposable syringe. The residual concentration of the ethoxylated surfactant was measured by high performance liquid chromatography fitted with an AMP C18 column. Methanol/water (90/10, v/v) was used as a mobile phase at 1 ml/min. The surfactant adsorption can be calculated using the following equation:

$$\text{Adsorbed amount} = \frac{v(C_0 - C_1)}{m} \text{ mg/g} \quad (1)$$

V= volume of the solution (L)

C<sub>0</sub>= initial concentration of the ethoxylated surfactant (mg/L)

C<sub>1</sub>= residual concentration of the ethoxylated surfactant (mg/L)

m= mass of the surfactant sorption structure (g)

Figure 1 illustrates the experimental results. There is no significant change in the adsorption capacity of the surfactant sorption structure at pH values less than 9, revealing that the surfactant sorption structure exhibits high sorption over a wide range of pH values. Nevertheless, a significant decrease in adsorption capacity is observed at pH values above 10.

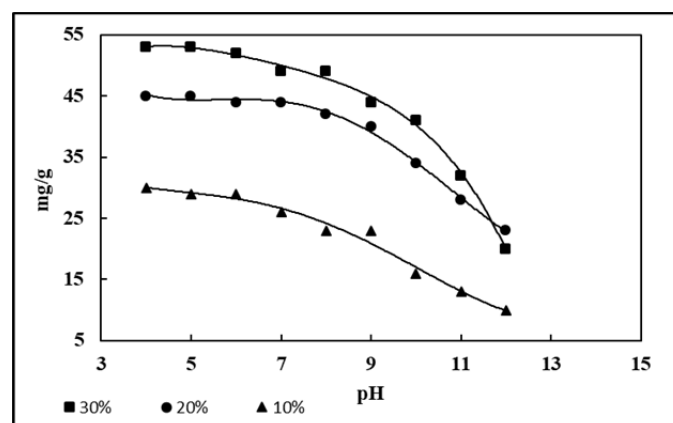


Figure 1: Effect of pH on the adsorption of an ethoxylated surfactant onto the surfactant sorption structure containing 10 wt%, 20 wt% and 30 wt% of the active pre-prepared composite at different pH values and at room temperature.

### Effect pH on the desorption of the ethoxylated surfactant

Figure 2 shows the release pattern of the ethoxylated surfactant at different pH values. Approximately 0.1 g of the freshly prepared powdered surfactant structure containing 30 wt% of the pre-prepared composite and 380 mg/g of the ethoxylated surfactant was mixed at a low shear rate with 150 ml of distilled water for 4 hours. The pH of the distilled water was adjusted using 0.1 M of NaOH solution. The released amount of the ethoxylated surfactant was calculated using equation (1). The ethoxylated surfactant was desorbed slowly at pH values below 9; however, about 64% of the adsorbed surfactant was desorbed at pH 11. This reveals that the initiation phase can be controlled by controlling the pH of the fluid.

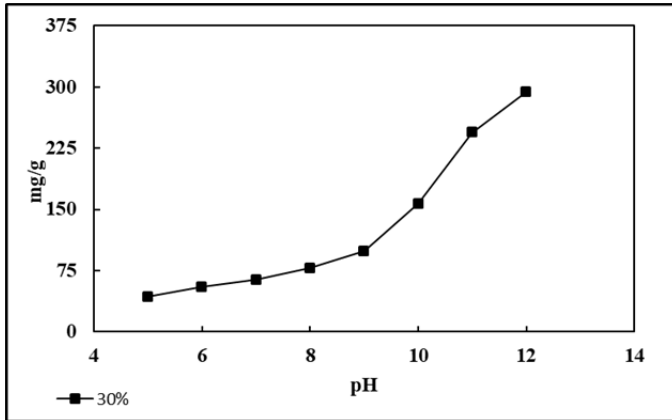


Figure 2: The release profile of the ethoxylated surfactant from a powdered surfactant structure containing 30 wt% of the pre-prepared composite at different pH values and room temperature.

### Effect of the surfactant sorption structure on the rheology of class G cement

The effect of the surfactant sorption structure on the rheology of class G cement blends with a density of 1901 kg/m<sup>3</sup> was determined using an OFITE 900 rheometer at 30°C and 50°C. The slurry was prepared by mixing dry cement, the surfactant sorption structure and Calgary tap water in a Waring blender according to API RP 10B-2 and conditioned for 20 minutes using an OFITE atmospheric consistometer at the given temperature. The concentration of the surfactant structure was 0.2 wt% and 0.4 wt%. It was found that the newly developed surfactant sorption structure had no effect on the rheological behavior of the cement slurries as shown in Tables 1 and 2.

Table 1: Effect of the surfactant sorption structure of the 1,901 kg/m<sup>3</sup> blend of class G cement at room temperature

SSS, wt%	T., °C	Shear rate, rpm					
		600	300	200	100	6	3
Neat	30	110	79	62	50	20	13
0.2%	30	109	79	60	49	22	12
0.4%	30	110	80	62	49	21	13

Table 2: Effect of the surfactant sorption structure of the 1,901 kg/m<sup>3</sup> blend of class G cement at 50°C

SSS, wt%	T., °C	Shear rate, rpm					
		600	300	200	100	6	3
Neat	50	108	84	71	59	22	14
0.2%	50	109	84	73	60	22	13
0.4%	50	110	83	72	60	23	14

### Effect of the powdered surfactant structure on foaming tendency

One of the major drawbacks of mixing the surfactant package with the aqueous-based spacer on-the-fly is the foaming tendency of the surfactant. Foaming tendency was evaluated using the density method. Two aqueous-based spacer blends containing several concentrations of the powdered surfactant structure were prepared using the API standard mixing schedule for cement. The spacer was mixed at a low shear rate (4,000 rpm) for 15 s and a high shear rate (12,000 rpm) for 35 s. The densities of the spacer blends were 1,400 kg/m<sup>3</sup> and 1,700 kg/m<sup>3</sup>, respectively. The density of the spacer was then measured immediately after mixing the spacer.

The densities of the top and bottom of the fluid in the mixing container were measured and the change in the density of the aqueous-based spacer was calculated, Table 3. Apparently the change in the density of the spacer was less than 5%, meeting the requirements of the spacer.

Table 3: Effect of the loading of the powdered surfactant structure on the density of the aqueous-based spacer

PSS, wt%	1,400 kg/m <sup>3</sup> spacer at 25°C			
	Top (Kg/m <sup>3</sup> )	Bottom (Kg/m <sup>3</sup> )	Diff.	Diff., %
Neat	1,322	1,345	23	1.7
1	1,310	1,325	15	1.2
1.5	1,285	1,312	27	2.1
2	1,274	1,321	47	3.7
2.5	1,280	1,332	52	4.1
3	1,290	1,329	39	3.0

1700 kg/m <sup>3</sup> spacer at 25°C				
PSS, wt%	Top (Kg/m <sup>3</sup> )	Bottom (Kg/m <sup>3</sup> )	Diff.	Diff., %
Neat	1,634	1,666	32	2.0
1	1,622	1,639	17	1.0
1.5	1,631	1,644	13	0.8
2	1,636	1,658	22	1.3
2.5	1,627	1,639	12	0.7
3	1,609	1,622	13	0.8

Using this powdered surfactant structures may thus be advantageously employed to prevent excessive foaming. The slow release of the chemical additives, including the surfactant blend, from the powdered surfactant structures into the treatment fluid reduces its surface tension. This causes the entrained bubbles formed while the treatment fluid is being agitated when mixed at a high shear rate and pumped downhole to move to the surface of the fluid. In addition, the polyol included in the surfactant sorption structure hinders lathering and prevents the entrainment of the gas in the treatment fluid.

#### Assessment of the wettability of the newly developed powdered surfactant structure

The wettability of the newly developed powdered surfactant structure was assessed using an OFITE 900 rheometer at 25°C and 80°C. The rotor was washed with distilled water and dried with acetone to ensure it was completely clean. The mud sample was conditioned at 25°C before being loaded on to the OFITE 900 rheometer. Tables 3 and 4 show the physical properties and rheology of the used mud, respectively.

The pre-conditioned mud was then loaded on to the OFITE 900 rheometer's cup and the rotor was set to spin at 100 rpm for 5 minutes. The aqueous-based spacer containing 1.8 wt% of the powdered surfactant structure was mixed using the API standard mixing schedule for cement and then loaded on to the OFITE 900 rheometer's cup immediately after mixing. The rotor was set to spin at 100 rpm for 10 minutes. Finally, Calgary tap water was loaded on to the OFITE 900 rheometer's cup and the rotor was set to spin at 100 rpm for 5 minutes. Figure 3 shows the mud cleaning results at 25°C.

Table 4: Physical characteristics of the used mud

Test	Unit	Result
Density	kg/m <sup>3</sup>	1310
HTHP @ 80°C	mL	4.2
Funnel Viscosity Retort	sec/L	137 s @ 20.0°C
	Oil:Water Ratio	84.3 : 15.7
	Oil	72.5
	Water	13.5
	Solids	14
Sand Content	% by volume	0.6
Chlorides	mg/L	34,000
Calcium	mg/L	25,600
Excess Lime	kg/m <sup>3</sup>	10.36
CaCl <sub>2</sub>	kg/m <sup>3</sup>	53.38
NaCl (Sol/Insol)	kg/m <sup>3</sup>	0
LGS	% by volume	7.3
	kg/m <sup>3</sup>	193.5
HGS	% by volume	5.6
	kg/m <sup>3</sup>	233.7

Table 5: Rheology of the used mud at 50 °C

Test	Unit	Result
600		57.8
300		33.6
200		24.8
100	D.R.	15.9
6		5.7
3		5.3
PV	mPa·s	24.2
YP	Pa	4.7
YP	lb/100ft <sup>2</sup>	9.4
10 Second Gel		6.5
10 Minute Gel	D.R.	9.2

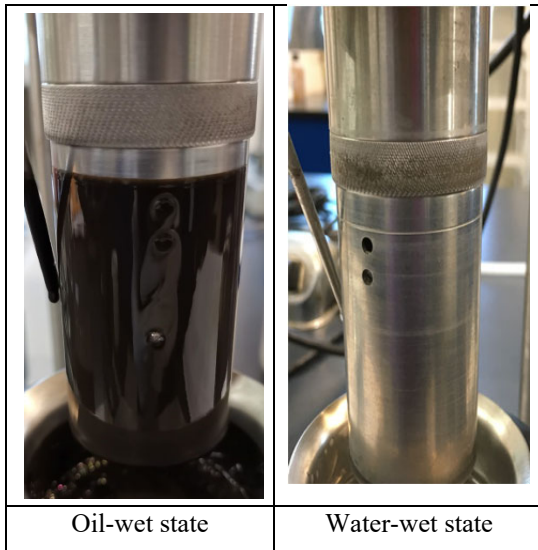


Figure 3: Mud cleaning results at 25 °C

The same experiment was repeated at 80°C using the same mud as in the previous experiment. A fresh spacer sample was prepared using the same protocol as in the previous experiment. The spacer density in both experiments was 1,400 kg/m<sup>3</sup>. Figure 4 shows the mud cleaning results at 80°C.

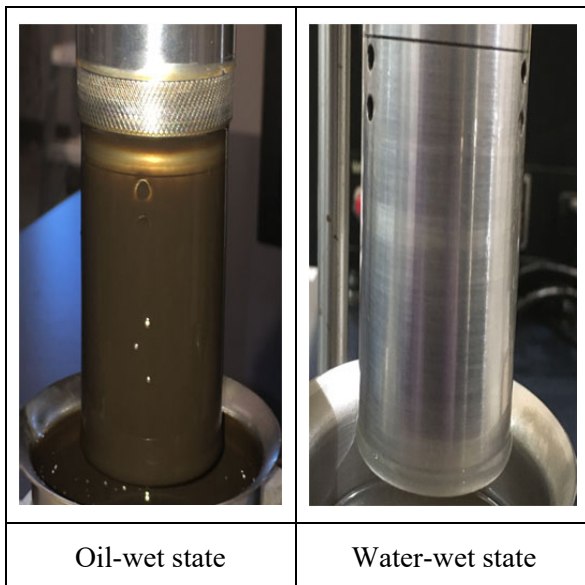


Figure 4: Mud cleaning results at 80 °C

## Conclusions

This study demonstrates newly developed powdered surfactant structures that comprise a novel surfactant sorption structure and an ethoxylated surfactant. We made the following findings:

- No significant change in the adsorption capacity of the surfactant sorption structure at pH values less than 9 was found.
- The adsorption capacity of the surfactant sorption structure decreases significantly at pH values greater than 10.
- The desorption of the ethoxylated surfactant from the powdered surfactant structures was pH-dependent.
- No excess foam was observed upon mixing the newly developed powdered surfactant structure with an aqueous-based spacer using the API standard mixing schedule for cement.
- The newly developed powdered surfactant structures efficiently removed OBM at different temperatures.

## Acknowledgments

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## Nomenclature

- OBMs* = Oil-based muds
- HAS* = High surface area
- SSS* = Surfactant sorption structure
- PSS* = Powdered surfactant structure
- HTHP* = High temperature and high pressure
- LGS* = Low gravity solids
- HGS* = High gravity solids
- PV* = Plastic viscosity
- YP* = Yield Point

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