

Performance Testing of Cement Defoamers

Allen Kelley, Kristina Fontenot, and Cornell Stanciu, Sasol Chemicals (USA)

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Abstract

In this paper we present the results of extensive cement defoamer testing. The testing compares silicone based, random EOPO, block EOPOEO, POEOPO block polymers, linear POEO ethoxylated alcohols, branched POEO ethoxylated alcohols in both commercial (US and European market) and experimental formulations. The initial base slurry's density (designed to be 12 ppg) will be compared to the final slurry density after the defoamer is added. By comparing the change in density of the initial slurry to the final defoamed slurry the effectiveness of the defoamer can be calculated. The results show how well each defoamer performs in the laboratory testing environment (1 atm, 70°C, API 10B-2 (5.3.4) cement mixing standards). Defoamers that produced densities closer to 12ppg can be assumed to have reduced foam the most. The mechanism by which these defoamers operate is explored and some of the limitations discussed. Each type of defoamer will be evaluated and compared to the other defoamers in their class and to the best performing defoamers in each other group. It is also shown that the systems physical properties dictate the defoamer that should be used within it and that developing new, less environmentally impactful defoamers for industrial purposes is a worthwhile venture. This paper is intended to help new engineers understand how defoamer chemistry works and show a very general overview of some testing methods, with a simple evaluation of a wide variety of commercial and experimental defoamers.

Introduction

The presence of foam in a cement blend is typically a design issue, caused by surface active or thin film forming admixtures. The most common "foaming agents" in the cement lab are fluid loss additives, dispersants and water reducers (Nelson and Guillot 2006). The need to redesign cement formulations for each well means that a single static design is impossible and that small variations from the original formulation can enhance the foam ability of the cement. This consistent tweaking of designs is almost unique to oil and gas and necessitates the use of "on the fly" defoamers.

The presence of entrained air in the cement slurry can cause a myriad of problems. One issue that arises when a cement slurry entrains air, is that as bubbles pass through the densitometer the true density of the liquid phase of the slurry is underreported. This makes the density of the liquid fraction

appear lower than it physically is. The incorrect density will be reported to the automated cement mixing system or operator, causing the addition of extra cement. This results in a denser slurry than designed with vastly different physical properties. If the overweighed slurry is allowed to reach the wellhead and get pumped downhole, one could have major wellbore issues or even a plugged well. Unexpected foam in cementing jobs can cause costly remedial cementing or even damage the formation. Even when foamy cement is properly placed the entrained bubbles in the slurry can migrate to the top of the cement column leaving an uncemented gap. This gap can cause pipe wag, broken piping, large overpressure issues and poor zonal isolation. Poor zonal isolation is often cited as the cause of environmental incidents (polluted ground water, methane leaking from wellbore and even erosion of the formation) related to oilfield activities.

By supposing that a cement defoamer needs to be fast acting in order to be effective in a continuous cement blending processes, the testing method used to mimic this process also needs to continuously entrain air similarly to the "Bikerman test", such that the efficiency limit of the defoamer can be tested. The testing method utilized is a modified version of a continuous foam rise method, where a standard cement blender cup, utilizing API 10B-2 (5.3.4) mixing standards are used to entrain the air. This method proved to be fast, reproducible and utilize common equipment found in cement testing labs.

Background

To understand how to choose a defoamer it is necessary to understand how the foam is forming, foam dynamics and methods of foam collapse. For this reason, a brief introduction into these topics will be presented.

Some cement additives interact at the liquid-vapor interface by reducing the surface tension, making it easier for the surface area of the liquid-vapor interface to be expanded by the entrained air. The hydrophobic regions of these materials reduce their energy through Van Der Waals interactions and by migrating to the liquid-vapor interface. The hydrophobic groups damage the surface tension by breaking the order imposed on the first few solvation shells of water at the liquid-vapor interface, this is done by disrupting the dipole-dipole and coulomb forces (Witten and Pincus 2004). These additives also tend to have anionic charged groups that are coulombically

attracted to the Stern layer of the cement particles. This often allows the additives to perform double duty by influencing the foam stability as well.

The physical interpretation of an aqueous foam is a complex and dynamic topic for most physicists and only gets briefly mentioned in select graduate classes. For this reason, the physical underpinnings of foam dynamics are generally not well understood by benchtop chemists or field engineers. Once formed, aqueous foams generally have four forces acting on them (Schramm 1994). Gravity causes drainage of the plateau regions and increases the capillary pressure in the lamellae and plateau regions. The capillary pressure gradient between the plateau borders and lamellae causes further drainage from the lamellae to the plateau borders. Pressure differences between the large and small bubbles and the solubility of the gas phase in bulk fluid cause gas molecules to migrate through the lamellae. This promotes the growth of larger bubbles and destroys smaller bubbles through a process known as Ostwald Ripening. The last force that affects foams is a coulomb repulsion term known as the electrical double layer. This is where the cell walls come into close enough proximity that the charge brought about by the surface can be felt by the opposing surface through the bulk fluid. Due to the large dielectric constant of water within a bilayer the surfaces must be in extremely close proximity in order to experience charge repulsion (Meneses-Juarez, Rivas-Silva and Gonzalez-Melchor 2018).

By tying this simple picture of foam dynamics to real world observations it is easy to see that there are basically two types of foam, transient and stable. Transient foams are characterized by their naturally short lifespans. In general, this is due to the foam ability and foam stability generated by the surface active agent in the bulk system. What this means is that the surface active agent's foam ability is large enough to generate unwanted foam, but the foam stability is low enough that the foam collapses before it affects the performance of the final product. In transient foams natural mechanical and thermal fluctuations within the lamella facilitate the formation of holes (Prud'homme and Khan 1996). This occurs through a few different mechanisms, mainly expansion of the surface area of the lamella by surfactant stabilization or through a low elasticity of the interface. In short transient foams fall apart due to inherent instabilities built into the surface active/bulk system. Stable foams are formed when the balance between foam ability and foam stability is optimized. Stable foams exhibit the ability to resist drainage, usually through viscosifying the fluid in the lamella and even reversing the flow of liquid as the capillary pressure increases. They manage the pressure gradient between the plateau and lamella regions such that fluid can be exchanged between the two as mechanical and thermal fluctuations occur. Ostwald Ripening is mitigated by having a higher critical packing parameter and the electrostatic repulsion between cell walls is strong enough that fluctuations in the pressure gradient of the lamella can't force the opposing cell walls close enough together to create a hole. (Exerowa and Kruglyakov 1998) In this type of system an external defoamer is needed to catalyze coalescence of the bubbles. There are typically three types of

defoamers used in cementing operations: silicone based, oil based and block copolymer (Fink 2012). These defoamers can be further broken into two categories, fast and slow acting. They all work off the mechanism of de-wetting or bridging of the lamella (Garrett 1993). This process involves a defoamer droplet becoming trapped in the lamella. For fast defoamers as drainage occurs the capillary pressure increases until the pressure becomes larger than the entry barrier of the oil droplet into the cell wall. The oil droplet enters the cell wall and forms a three-phase interaction, oil/water/air where the adhesive force between the aqueous bulk and the oil can be significantly reduced when compared to the water-water interactions. This allows a rapid expansion of the surface area of the bubble "de-wetting of the surface" as the cell wall attempts to reach a 90° angle between the aqueous bulk and oil phase (Garrett, Preliminary considerations concerning the stability of a liquid heterogeneity in a plane-parallel liquid film. 1980). This also creates a weak spot for mechanical and thermal fluctuations to thin the lamella. If the lamella becomes sufficiently thin the droplet will pierce both opposing cell walls forming a "bridge". At this point the adhesive character between the aqueous and oil phase becomes very important, because if the oil/water interactions are too strong then the water will wet the surface and the hole must be created by forcing the oil droplet to split "bridge deformation" due to the force of the mechanical or thermal fluctuations exceeding the cohesive energy of the oil/oil interactions. If the oil/water interactions are weak then both cell walls will attempt to reach the 90° angles and coalesce. This process can be seen in Figure 1. If the defoamer is slow then as the drainage occurs and the capillary pressure increases the oil droplets are pushed into the plateau regions where they slow the drainage process. Eventually the capillary pressure may increase above the entry barrier energy of the oil droplets and they will pierce the cell wall at the plateau regions, creating a hole and coalescing the bubbles (Koczona and Wasan 1994).

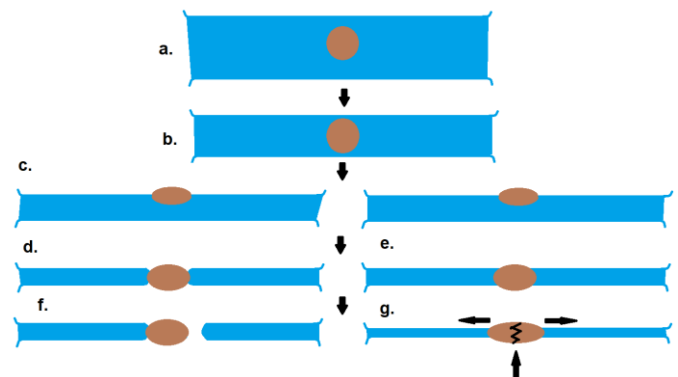


Figure 1: a) Shows a defoamer droplet in the lamella. b) Shows a defoamer droplet in the lamella as drainage increases the capillary pressure and the lamella thins. Capillary pressure < entry barrier energy c) Shows a defoamer droplet in the cell wall as drainage occurs and the capillary pressure increases. Capillary pressure > entry barrier energy d) Drainage has reduced the thickness of the lamella such that the droplet penetrates both cell walls. The adhesive forces between the water and the droplet are very small and the cell wall oscillates on the surface of the oil drop attempting to create a 90° angle. e) Drainage has reduced the thickness of the

lamella such that the droplet penetrates both cell walls. The adhesive forces between the water and the droplet are strong enough for the water to wet the surface. f) Normal thermal or mechanical fluctuations in the lamella oscillate the cell wall enough that they contact each other and coalesce the bubbles. g) Continued drainage of the lamella increases the capillary pressure, where normal oscillations in the lamella rupture the oil droplet allowing coalescence to occur.

Silicone defoamers tend to have hydrophobic solids entrained in the oil. These solids have been shown to migrate to the interface, reduce the entry barrier energy and speed up the de-wetting of the oil drop (Dippenaar 1982).

Experimental

A 12ppg slurry was designed (Table 1) and blended using API 10B-2 (5.3.4) standards. This blend was designed to entrain excess air at room temperature during mixing. The cement was added to the blender cup within the first 15 seconds of low shearing. It is assumed that with a uniform cement blend and mixing procedure that the blender cup will entrain air at a uniform rate, over all the trial runs. The density of the resulting cement will then be dependent upon the rate of foam creation in the system minus the rate of foam collapse. Once the blender stops shearing the gel strength and density of the cement keep the bubble migration to a minimum. A top down picture of the foam blend was taken directly after blending in order to compare visually to the other initial cement blends and cement with defoamer added. After the picture the blender cup was immediately started again and 1 drop of defoamer was added. Immediately after the shear finished a second picture was taken, and the density determined. The visual inspection highlights the ability of the defoamer to reduce surface foam. The density of the slurry bulk was determined by the weight difference between an empty 100 ml graduated cylinder and a cylinder with 100 ml of cement. It must be noted that small errors can occur with this method, where the cylinder can be slightly over or under filled. To account for this, the procedure is repeated 3 times and the average densities are reported, all density measurements were required to be within $\pm 0.20\text{g}$. The choice not to use a pressurized fluid density scale to determine the foamed slurries density, was deliberate. By adding pressure to the foamy cement, the size of the foam cells will be altered, and this would add more error into the final density calculations. There were also concerns about sampling, because the injected cement would not be uniform from run to run.

Table 1: 12ppg Room Temperature Cement Design

Component	Percent Composition
Type I/II Cement	45%
Pumice	45%
Bentonite Gel	10%
Polyvinyl Alcohol	2%

Results

In order to qualify the different defoamers, a testing

methodology was created and elaborated on in the “Experimental section”. The designed density of the cement blend is 12.0 ppg (Table 1), while the actual density measured after blending was 9.96 ppg. This is because the foam has displaced some of the cement in the graduated cylinder. After the addition of defoamer the cements density should increase to 12.0 ppg. In the data below, the pictures on the left are used as a reference and contain no defoaming agent, the picture on the right has 1 drop of defoamer added. These pictures are chosen such that a general visual inspection of surface foam can be seen at the density of cement reported. Not all of the pictures for each test are shown, but a general idea of what the cement looked like can be gained by looking at the difference between groups of pictures. The results are shown from the best defoamer to the worst, the one that takes the density from 9.96ppg to the highest density first. The tables display information on the classification of defoamer, final density after addition of defoamer and whether the defoamer is commercially available or being developed in the laboratory.



Figure 2: (Left) 9.96ppg cement without defoamer. (right) 12.00ppg cement after 1 gpt of defoamer.

Class of Defoamer	Density after 1 gpt of Defoamer (ppg)	Experimental or Commercial
Branched POEO alcohols	12.00	Experimental
Branched POEO alcohols	12.00	Experimental
Linear POEO alcohols	12.00	Experimental
EOPOEO	12.00	Commercial
Oil base	12.00	Commercial

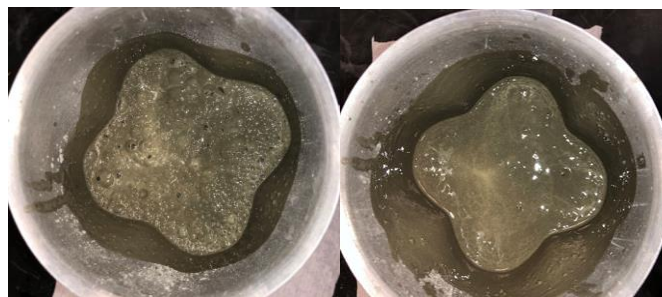


Figure 3: (Left) 9.96ppg cement without defoamer. (right) 11.80ppg cement after 1 gpt of defoamer.

EOPOEO	11.80	Commercial
Silicone	11.76	Commercial
Linear POEO alcohols	11.69	Commercial
Silicone	11.12	Commercial



Figure 6: (Left) 9.96ppg cement without defoamer. (right) 8.52ppg cement after 1 gpt of defoamer.



Figure 4: (Left) 9.96ppg cement without defoamer. (right) 10.61ppg cement after 1 gpt of defoamer.

Silicone	10.61	Commercial
Silicone	10.60	Commercial
Silicone	10.40	Commercial
Silicone	9.78	Commercial



Figure 5: (Left) 9.96ppg cement without defoamer. (right) 9.32ppg cement after 1 gpt of defoamer.

EOPOEO	9.32	Commercial
Random EOPO	9.20	Experimental
POEOPO	8.84	Commercial
POEOPO	8.52	Commercial

Conclusions

Unwanted foam in cement blends is a problem, and not being able to predict, diagnose the causes of and easily test solutions to cement foam issues can have serious negative consequences in the field. Here we presented an interesting idea that by focusing on the penetration energy and internal molecular cohesive forces of fast acting defoamers, that a continuous air entrainment mechanism would be needed to provide data on the performance of cement defoamers. By utilizing the most basic laboratory equipment (blender assembly, balance and graduated cylinder) a simple dynamic testing method that quickly and easily showed the difference between multiple defoamers was developed. This technique was used to test a wide range of defoamers on a specific cement blend. It was shown that for this blend linear and branched EOPO alcohols, specific POEOPO blends and base oils with high hydrophobicity and low cohesive forces increased the density the most. The addition of most silicone defoamers had little effect on the foam. The thin film forming PVA coupled with the large volume of solids in the lamella increased the entry barrier energy and reduced the ability of the defoamer to pierce the cell wall and de-wet the surface (Denkov 2004). The miscellaneous EOPO products that decreased the density of the cement acted in fact as foamers. This harkens back to the cement design, the PVA coupled with a relatively viscous high solids cement generated the foam. If the PVA is removed then the foam issue stops, however PVA is not surface active, it is thin film forming. The EOPO defoamers tested are unable to penetrate the cell wall and become trapped in the plateau regions. Once trapped they slow drainage and stabilize the foam. It must be noted that this “trend” shown here is only valid for this cement blend and that changing the blend can dramatically shift the performance of each individual defoamer class. In conclusion each cement foam is physically different with different penetration energies and wetting profiles, however by using this fast and easy method the best defoamer candidates can be narrowed down extremely efficiently.

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Nomenclature

- PVA = Polyvinyl Alcohol
gpt = gallons per thousand gallons

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