Foams are stabilised dispersion systems containing gas as the dispersed phase and a liquid or solid or a mixture of both as the continuous phase. Most chemical additives needed to make cement slurries are surface active molecules with an amphiphilic structure; on one hand soluble and on the other insoluble (or of limited solubility) in aqueous phase. This surfactancy is responsible for the stabilisation of air-liquid interfaces and the potential generation of excessive foam and air entrainment as shown in Figure 1. Such additives include cement retarders, dispersants, fluid loss control additives, gas migration control agents and ductility improvement additives. Chemicals used to enhance cement grinding are also known to cause foaming to some extent.

Cement foaming, chemically entraining air in cement slurries to account for additives involved, is difficult to categorise in the sense of a conventional process. It can be viewed as an emulsion of air in the cement - water system or foam formation in the liquid phase and retained by the gel or solid network, or both. Origins of air in cement slurries include air already contained in the system and air entrapped during mixing. Reviewing literature on air entrainment revealed that it is clearly a complex process, which is affected by many factors such as the mixing regime, physical and chemical properties of oil well cements, water ratio and quality, dosage and properties of the foaming agent, other chemical additives and supplementary cementitious materials (SCMs), and a range of other parameters.

In well cementing applications, the reliable administration of defoaming chemistries is a key step in preventing excessive foaming and avoiding operational difficulties due to entrained air. Traditional products that have been used in common operating conditions, often pose a risk to the environment. A new generation of ‘greener’ chemistries is needed either in liquid or dry forms to meet industry and environment regulations. Solid defoamers represent a particularly attractive alternative, as they are characterised by long term stability and ease of handling under severe climatic conditions.

**Challenges with environmental regulations**

Compliance with national and international environmental regulations governing use and discharge of oilfield chemicals is a critical factor in the development of new, environmentally-acceptable chemicals. The most important institutions guiding these regulatory frameworks are (1) the US Environmental Protection Agency for US Gulf Coast/ Gulf of Mexico and (2) the Oslo/Paris Commission (OSPARCOM) for North Sea and other European Countries. The OSPAR commission defined a very restricted list of substances that are considered to Pose Little Or No Risk (PLONOR) to the environment; some countries follow the guidelines more rigorously than others. Most of the service companies supply their customers globally; the need for greener technologies becomes a requisite to operate, as many state oil companies and international companies are looking into the North Sea regulations when establishing their environmental controls and legislations.

For the last few decades, the development of greener chemistries for well completion fluids has become more challenging due to...
necessary high performance standards and evolving restrictive regulations. Although one of the additives with the lowest dosage rate, defoamers and antifoams represent a particular challenge when looking into formulations with more environmentally-viable materials. There is a tendency to shift from non-biodegradable silicone based products. Non-silicone chemistries such as fatty alcohols, esters and phosphates that show less toxicity and better biodegradability, may represent viable solutions. However, the challenge of achieving a high performance and cost-effective product remains, especially as technological needs on the field become more strict and demanding. Kemira Chemicals is working toward oilfield chemicals that meet strict global product safety requirements and promote greener, alternative chemistries without compromising performance under field conditions.

Using a systematic approach, different defoamer chemistries were evaluated for highly foaming systems. A series of non-toxic, biodegradable (more than 60%, OECD 306) and highly efficient products were developed achieving ‘yellow’ banding for Norway and ‘gold’ for UK applications. In addition, a ‘Smart’ solid substrate with ‘green’ PLONOR banding was developed to be used as a carrier for the above chemistry. The ‘Smart’ dry technology is proving to be highly efficient and could open new perspective for the development of greener and even more cost-effective defoamers for cementing applications.

As shown in Figure 2, the process for development of green defoamers involves a systematic study and evaluation of active defoaming chemistries, formulating agents and diluents or carriers. Performance testing is also a key in development of green products since it defines the effectiveness of final products particularly when it mimics field and operating conditions.

Testing methods for defoamers

There is currently no API standard for evaluation of defoamers for oil and gas cementing. Cementing service companies often use their own developed lab procedures, which often includes:

- Slurry preparation using API procedure.
- Measuring slurry density using a mud balance or other methods.
- Visual investigation of air-entrainment in cement for voids and channels.
- Effects on other properties such as rheology, thickening time and compressive strength.
- Comparison of performance against a defoamer currently used in the field as a benchmark.

A controlled approach has been developed for the evaluation of cement defoamers using a unique Foam and Entrained Air Test analyser (FEAT) and a more comprehensive blender foam test method that provide more insights into cement foaming and defoaming processes. More detailed description of the methodologies used can be found in the ‘References’ section of this article (Mahmoudkhani, 2011).

The blender test was designed to address the effect of shear rate, slurry volume and time on foaming during mixing of cement slurries. A clear protocol to evaluate densities of foamed slurries allow for much controlled testing and better reproducibility of the data. The FEAT technique utilises a fluid recirculation loop designed to dynamically measure fluid foaming/defoaming characteristics.

**Table 1. Defoaming chemistries and their discharge conditions**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Discharge permits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicone A</td>
<td>No</td>
</tr>
<tr>
<td>Silicone B</td>
<td>No</td>
</tr>
<tr>
<td>Non-silicone C</td>
<td>Yes (‘Yellow’ for Norway, ‘Gold’ for UK)</td>
</tr>
<tr>
<td>Non-silicone D</td>
<td>Yes (‘Yellow’ for Norway, ‘Gold’ for UK)</td>
</tr>
</tbody>
</table>
The instrument is temperature controlled, open atmosphere, and features an inline foam generation chamber to entrain air in the experimental media. Density is continuously recorded using a density flow meter once recirculation begins. The effect of additives such as foamers, defoamers and antifoamers may be determined at any time by injection into the foam chamber. Figure 3 represents a schematic of the defoamer density–time curve obtained by the FEAT Technique. The curve consists of several distinct areas. The first portion of the curve with a downward slope (\(d_{\text{init}} \) to \(d_{\text{min}}\)) indicates the quickness with which the test media entrains air and foams. Defoamer is then injected at a chosen density or time noted on the graph. The initial density minimum (\(d_{\text{min}}\)) of the graph represents the time which the defoamer has begun to affect the media. The upward slope from this minimum (\(d_{\text{min}} \) to \(d_{\text{max}}\)) represents the quickness with which the defoamer acts upon the media to remove entrained air. The curve then generally peaks at the defoamer’s maximum effectiveness (\(d_{\text{max}}\)). An ideal defoamer would maintain the same density as the peak, whereas a real defoamer gradually loses effectiveness causing the curve to drop as the defoamer becomes emulsified into the test media.

**Performance evaluation**

As discussed earlier, a careful evaluation of the effectiveness of a product, either as an anti-foaming or defoaming agent, should reflect the mixing conditions and dosage practice in the field. This systematic evaluation requires separate testing under the different conditions. Both FEAT and blender tests were utilised here; while blender test evaluates defoamer capability on a cement slurry, FEAT analysis looks at the liquid mixing step prior to slurry creation. Non-silicone ‘green’ chemistries are then benchmarked to traditional silicone products.

Figures 4 and 5 show the blender and FEAT results for cement slurries with a gas mitigation control additive (a latex type product). For such a highly foaming latex, the selection of non-silicone products will be more effective than silicone chemistries and in particular a better option when defoaming properties are needed in the liquid mixing step prior to slurry creation.

Various fluid loss additives are routinely used in preparation of cement slurries. They are often used at higher dosage in lightweight and ultra-lightweight cement slurries to provide adequate properties and controlled fluid loss during placement in the borehole. Performance of silicone and non-silicone defoamers is evaluated for cement slurries containing a fluid loss additive: polyvinyl alcohol (PVA). As shown in Figure 6, silicone based defoamers were found to be not effective in PVA foaming systems, instead both non-silicone based defoamers exhibit superior performance as indicated by measured slurry density in comparison to the design density.

**SMART dry defoamers**

Liquid defoamers are predominantly used in normal operating conditions, but dry defoamers are preferred in extreme climates, mainly due to ease of handling and storage, long term stability and uniformity. In dry defoamers, the active defoaming chemistry is loaded on the voids of a high surface area (solid) substrate. Consequently, the development of dry defoamers brings another level of complexity associated with the adsorbent structure which strongly impacts defoamer release and subsequent performance. Although high surface area substrates (such as precipitated silica) are often chosen due to their high adsorption or loading capacities, they may lack performance owing to poor and slow release of the active defoaming chemistry from the substrate and thus lead to product misuse (sacrificial defoamer).

A careful selection of a substrate and active defoaming agent should address several aspects ranging from environmental performance evaluation

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**Figure 5.** FEAT analysis of silicone and non-silicone chemistries in the latex system.

**Figure 6.** Blender foam test data for API Class G Cement and PVA (0.9%) system. All defoamers are dosed at 0.2% BWOC.

**Figure 7.** Formulation of dry defoamers, effect of substrate structure on defoamer adsorption and release.
The ‘green’ non-silicone defoamer was formulated and studied in its liquid form (‘Liq’) and in two dry forms: one adsorbed on a traditional highly porous substrate (‘Dry’) and a second one adsorbed on a low porous ‘smart’ substrate expecting faster release of the active (defoamer) from the substrate (‘SD’). Figure 8 shows the blender foam test results for dispersant and salt system at different dosages. It is noticeable how the liquid and ‘smart defoamer’ sample remains highly efficient compared to the conventional dry product. This data proves the significant effect of the substrate structure on the release and hence, the superior performance of the Smart dry defoamer.

Conclusions
As local environmental legislations are under constant revision, it is important to develop new products considering not only current but also future needs. The technical constrains represent a true challenge when chemical companies need to formulate effective technologies limited by environmentally-viable components. The new dry technology was proven to be highly beneficial, granting all the advantages of dry products plus flexibility in terms of dosage practices. The key to the future is finding ways to do more with less.

References