

Cementing Additives Designed for Offshore Applications

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ABSTRACT

With demand for oil and gas at an all-time high, exploration of offshore sites has become increasingly popular. In addition, environmental sensitivity has become an ever-growing issue for these wellsites over the last 20 years. Regulations and standards have coincided with these environmental concerns and have continually become more stringent on the chemicals that can be used when cementing a well. To adhere to the environmental guidelines, new chemical additives are needed that are biodegradable, non-accumulating, and non-toxic.

This paper will discuss the regulations of the North Sea because they are typically the most proactive and stringent of all environmental regulations in force. Also discussed are the latest advancements in cementing additives that meet the environmental requirements of the North Sea. A retarder, fluid loss additive, dispersant, and foamer have been developed that meet these requirements. Each of these additives exhibits an increased environmental compliance in addition to a technical advantage with oilwell cementing. Ecotoxicological data and performance data are presented for all of these cementing additives.

INTRODUCTION

In the areas surrounding the North Sea, there have been rising concerns surrounding the preservation of environmental quality. In response, the Oslo-Paris Commission (OSPARCOM) was formed with the objective of protecting the marine aquatic environment in the Northeast Atlantic. In an attempt to reduce environmental costs, the OSPAR commission established guidelines that must be met by any chemicals that are intended for use offshore. Stringent testing protocols are used to evaluate chemicals that could potentially be detrimental to the marine environment.

This is monitored by the Harmonized Mandatory Control System (HMCS), which is essentially the process that governs the progression of each company through OSPARCOM's required steps (1). The HMCS has four aspects, which include generating environmental data for the product, reporting of this data according to the appropriate authorities, assessing the product according to a prescreening scheme, and finally submitting the subject to Chemical Hazard Assessment and Risk Management (CHARM).

The reporting of the environmental data of each project is summarized by the Harmonized Offshore Chemical Notification Format (HOCNF) (2). This format includes a mandatory form that questions the data on biodegradation, bioaccumulation, toxicity, and several other factors that might provide an insight into substances being used. Typically, materials that appear on Annex 5 of the OSPAR strategy (mutagens, carcinogens, reprotoxins, etc.) are denied use (3). Each company must complete this form before applying for a discharge permit in any area governed by the OSPARCOM. However, substances that have been tagged with a "Pose Little or No Risk" (PLONR) rating are exempt from this requirement because they do not require further testing (4). These tagged chemicals may be used and discharged anywhere in the North Sea without further environmental evaluation.

The prescreening process (Figure 1) requires two of three conditions to be met for a substance to be ranked with the CHARM model (5):

1. The substance's tendency to bioaccumulate is assessed by procedures specified by the Organization for Economic Cooperation and Development (OECD). Materials that have a resulting $\text{Log}(P_{ow}) < 3$ are tagged non-bioaccumulating. Those materials with results greater than 3 do not meet this condition.
2. Biodegradation also has a procedure set by the OECD 306 marine saltwater testing. Materials must have results of greater than 60% to meet this condition. However, all substances must pass the initial criteria of >20% biodegradation (6).
3. LC_{50} or $\text{EC}_{50} > 10$ mg/l for all test organisms.

The service company's objective is to meet the stringent guidelines set forth in the Northeast Atlantic. This paper provides a summary of the most recent research in oilwell cementing applications, focusing on environmentally acceptable research.

PRODUCT DEVELOPMENT

The life and success of an oil well is highly dependent on competent zonal isolation. Zonal isolation refers to the process of placing cement in an annulus between the casing and the formation. The cement serves two primary functions:

- 1.) support of the inner casing from collapse or burst
- 2.) isolate multiple zones by preventing the movement of formation fluids or gases from one region to another. It also directs the produced hydrocarbon (oil or gas) through the casing to the surface.

To properly place a cement in the annulus, a wide variety of additives are used. These additives consist of retarders, fluid loss materials, dispersants, foaming agents plus numerous others.

Retarders are used to control the set time of the cement as the placement time and temperature vary from job to job. Fluid loss additives are used to minimize the amount of water lost from the slurry to a permeable formation. A loss of water can significantly affect the designed chemistry, as well as allow unwanted fluids from the formation to enter the wellbore. Dispersants are used to lower the viscosity of the cement slurry, allowing for a more mixable and pumpable slurry without increasing the water content. Lastly, foaming agents are used to entrain a gas to lower the final density of the slurry. The density is critical as the hydrostatic pressure of the column of cement can cause the formation to break down. A break down in the formation can result in lost circulation and the possibility of preventing the cement from being placed as designed. All of these additives are judged by their toxicity and ability to biodegrade and/or bioaccumulate. Although all of these additives must meet these requirements, all face different challenges based on their chemical makeup.

Retarders historically have been simple organic molecules or have been derived from a lignosulfonate polymer. These materials typically have low toxicity, some biodegradation, and low bioaccumulation. These characteristics are good for offshore applications, but many of these retarders are not very robust when it comes to temperature range. The challenge is to design a retarder that has the necessary qualities for use in the North Sea, but also has a large effective temperature range.

Foaming agents are typically composed of surfactants or mixtures of surfactants. Because of the nature of surfactants, their bioaccumulation is difficult to measure. Surfactants tend to be present in both the water and octanol layers in the bioaccumulation experiment. Also, the surfactants' ability to bind to surfaces, such as a cell wall, can lead to high toxicity of many aquatic organisms, which in turn leads to low biodegradation. This compounds the problems when designing acceptable foaming agents.

Fluid loss materials are typically high molecular-weight polymers. However, they are usually very soluble in water, which leads to low bioaccumulation. Because of their higher molecular weight, toxicity is typically low because the fluid loss material cannot pass through the cell walls of the aquatic organisms. Biodegradation is a concern because of the chemical nature of the fluid loss material and its high molecular weight.

Many of the same challenges faced when using fluid loss materials are also present when using dispersants. They are typically lower molecular weight polymers. This tends to help with

the issue of biodegradation; however, the dispersant material is easier for the aquatic organisms to absorb.

CURRENT PORTFOLIO

Environmentally Compliant Retarder

To have successful placement of cement in a wellbore, the thickening-time or set-time should be controlled. This is accomplished by adding retarders to the cement slurry, which delay the hydration of cement. Retarders are usually organic compounds that can range from simple organic acids to complex polymers.

Even though the chemistry of retarders might seem to be simple at first glance, the complexity of retarding the cement becomes evident when the temperature is increased. These simple organic acids might perform very well at temperature below 200°F, but they begin to degrade or become ineffective at temperatures above 200°F. This necessitates developing an environmentally acceptable retarder that can perform at elevated temperatures. Typically, high-temperature retarders that work at greater than 200°F are polymeric. This can lead to biodegradation and bioaccumulation problems as discussed earlier. The goal is to find or derive a retarder from naturally occurring materials. This approach has been successful and the toxicity data for this retarder can be seen in Table 1.

In Table 2, the environmentally compliant retarder (Retarder A) performs very comparably to a preferred retarder (Retarder B) that cannot be used in the North Sea. In nearly every instance, Retarder A has a longer thickening-time than Retarder B with similar amounts of each retarder being used. This fact alone shows the robustness of Retarder A. Another key characteristic of Retarder A is its ability to work over a large temperature range. The range for which Retarder A can be used is from 80°F to over 250°F. Because of this large temperature range, Retarder A can be used by itself without the aid of another retarder. This allows for extreme flexibility in slurry design as well as slurry stability because fewer additives are required to place the cement.

Environmentally Compliant Foaming Agent

As previously mentioned, many times the fracture gradient of the formation requires that the density of the cement slurry be reduced. This reduction in density lowers the hydrostatic pressure of the column of cement, ultimately reducing the applied pressure on the formation. The reduction in density can be accomplished in several different manners: additional water, hollow glass sphere, and/or entrained gas.

Water having a specific gravity of unity is the cheapest and easiest way to extend a cement slurry (reduce the density). Unfortunately, the addition of excess water has several detrimental effects on a cement slurry. Excess water can cause slurry instability issues when the cement goes static in the wellbore. Solid particles in the slurry can range from 1 to 5.0 SG. Thus, a low-viscosity slurry may allow extreme settling. In addition, water-extended slurries typically have greatly reduced compressive strengths. Compressive strength is required to support the casing during extreme wellbore operations and conditions.

Hollow glass beads provide for a second method of reducing the slurry density. Hollow glass spheres can range in specific gravity from 0.6 all the way down to 0.32. These are

technically superior to water-extended slurry. Though the hollow spheres do not contribute positively to the compressive strength, they have a much less negative impact than water extension on the ultimate compressive strength of the slurry. There are disadvantages to the use of glass spheres. Cost is a primary reason, as they can contribute significantly to the overall cost of a cement slurry (up to 50%). In addition, they have operational issues such as segregation and mixability of the slurry. The lightweight bead has a tendency to segregate to the top of a blend during transport, and may increase the viscosity of the slurry such that pump rates are hindered.

The third available method to reduce the density of a slurry is the entrainment of nitrogen into the slurry. The entrained gas can significantly reduce the density. Typically the slurry is entrained with 15 to 25% nitrogen (termed foam quality). Financially, the major impact is from the cost of the equipment to properly pump, meter, expand, and control the nitrogen system. The gas is entrained through the use of a foaming agent. The foaming agent can entrain gas and reduce the amount of gas that is allowed to break-back or escape from the slurry. The foaming agent is expected to capture and retain (stability) the necessary amount of gas until the cement can cure. In addition, it should not significantly delay (or accelerate) the time during which the slurry is pumpable nor hinder the ultimate compressive strength of the cement.

Table 3 compares the top technically preferred non-environmentally acceptable foaming agent (Foamer B) within the chemical portfolio against the recently developed environmentally acceptable foaming agent (Foamer A). The stability of the slurry is measured by recording the density of three sections of a cured sample top, middle, and bottom. A maximum density variation of 0.5 ppg or 5% is preferred. In addition, the thickening times of the two samples are noted, as well as the ultimate compressive strength of each. Results indicate that a reasonable pump time can be achieved and controlled, and the ultimate compressive strength is more than adequate for proper zonal isolation. The time to foam is critical as the mixing time (or energy input) is limited in field operations. Thus, an appropriate target for the lab is 10 to 15 seconds.

In addition to comparable or better performance than its non-environmentally acceptable counter-part, the new foaming agent is also capable of foaming freshwater, seawater, and saturated saltwater (NaCl). This indicates a more robust product because it can be used in a much wider array of applications. Table 4 depicts how the new foaming agent is superior in a salt-saturated environment (37% NaCl). It can be used in lower concentrations of potassium chloride and calcium chloride.

Operationally, the environmentally acceptable foamer is used in the standard concentrations (1-3% BVOW). Therefore, the footprint and logistics remain unchanged. Field trials have been conducted in several regions throughout the world. All users have reported back that the performance went as designed. Field reports indicate greater stability, less return of nitrogen to surface, and increased gas-migration properties. Table 5 provides results for applications in an array of cement designs (standard, fly ash, high-aluminate cement, and high-fine-particle system).

Environmentally Compliant Fluid Loss Agents and Disperants

Fluid loss agents help control the liquids present in the cement slurry. Without these agents, the fluids of the cement slurry could be lost to the formation, resulting in unhydrated cement, or worse, flash-setting cement. There are many other concerns with fluid loss control, but this paper does not focus on them.

As mentioned earlier, fluid loss agents typically are high-molecular-weight polymers. This has advantages and disadvantages with respect to biodegradation, bioaccumulation, and toxicity. As seen in Table 6, the environmentally compliant fluid loss agent (Fluid Loss A) has better or comparable fluid loss control than a fluid loss agent that can no longer be used in the North Sea (Fluid Loss B) (7). Fluid Loss A has a very robust temperature range without sacrificing performance.

Dispersants are additives that help control the viscosity of the cement slurry. Without these additives, many cement slurries could not be used in real-world situations because of surface mixing difficulties and the added force it would take to place a highly viscous slurry. Dispersants are typically polymeric materials with relatively low molecule weights when compared to fluid loss agents. However, like fluid loss agents, they face many of the same environmental challenges.

As can be seen in Table 7, Dispersant A compares very well with Dispersant B (7). Again, Dispersant B is a material that can no longer be used in the North Sea. Both have similar effects on the viscosity of the slurry and can handle similar conditions.

CONCLUSIONS

Environmental compliance has become a major topic of discussion and has become the responsibility of every person and corporation. Previously, it was thought that environmentally acceptable products would sacrifice technical performance and/or result in an elevated cost. This is no longer the case, as companies have dedicated significant resources specifically to the development of such chemicals. A technically superior retarder and foaming agent have been presented in this paper. These two products help round-out a product portfolio that allows for operation in some of the most environmentally stringent areas. This portfolio is not complete. Future research and effort should continue to expand the portfolio as well as push the limits of current chemical knowledge.

Table 1. Ecotoxicological Profile for Retarder A and Foamer A.

Product	Biodegradation (after 28 days)	Bioaccumulation	Toxicity
Retarder A	88%	<0	Non-toxic
Foamer A	70%	<3	Non-toxic

Table 2. Performance Comparison of Retarder A and Retarder B.

Product	Amount (%BWOC)	Temperature (°F)	Thickening Time (hr:min)
Retarder A	0.15	135	5:32
Retarder B	0.3	135	3:08
Retarder A	0.3	165	5+
Retarder B	0.3	165	4:15
Retarder A	0.3	194	2:38
Retarder B	0.3	194	3:38
Retarder A	0.2	203	6+
Retarder B	0.2	203	4:38
Retarder A	1.0	246	5:44
Retarder B	1.0	246	4:47

Table 3. Comparison of Foamer A and Foamer B.

Product	Time to Foam (sec)	24 hr Compressive Strength (psi)	Density (ppg)*		
			Top	Middle	Bottom
Foamer A	10	540	10.26	10.25	10.34
Foamer B	10	495	10.12	10.09	10.4

* Target density 11.0 from 15.8 ppg. Lab system can pull in excess air, resulting in extra entrainment.

Table 4. Salt Saturated Comparison of Foaming Agents.

Product	Time to Foam (sec)	24 hr Compressive Strength (psi)	Density (ppg)*		
			Top	Middle	Bottom
Foamer A	15	621	10.25	10.12	10.07
Foamer B	15	1106**	13.46	13.42	13.77

*Target density 11.2 from 17 ppg. Lab system can pull in excess air, resulting in extra entrainment.

**Higher CS as a result of not reaching target density.

Table 5. Results of Foamer A in a variety of applications.

Product	Target Density (ppg)	Time to Foam (sec)	24 hr Compressive Strength (psi)	Density (ppg)*		
				Top	Middle	Bottom
Fresh water	10.9	5	961	10.54	10.34	10.38
Seawater	10.3	5	1081	10.11	10.05	10.15
37% NaCl	10.8	6	698	10.63	10.39	10.51
Fly ash	10	10	651	9.93	9.88	9.94
High aluminate	11.0	10	331	11.22	11.32	11.46
High fines	9.8	5	801	9.94	9.85	9.98

* Target density 11.0 from 15.8 ppg. Lab system can pull in excess air, resulting in extra entrainment.

Table 6. Performance Comparison of Fluid Loss A and Fluid Loss B.

Product	Amount (%BWOC)	Temperature (°F)	Fluid Loss (mL/30 min)
Fluid Loss A	0.66	100	52
Fluid Loss B	0.66	100	88
Fluid Loss A	0.22	104	74
Fluid Loss A	0.55	104	30
Fluid Loss A	1.00	122	12
Fluid Loss A	0.22	140	98
Fluid Loss B	1.50	140	62
Fluid Loss A	0.66	149	34
Fluid Loss A	1.10	149	30
Fluid Loss A	1.32	149	26
Fluid Loss B	1.50	149	160
Fluid Loss A	0.77	180	84
Fluid Loss B	2.50	180	54
Fluid Loss A	0.77	190	40
Fluid Loss A	0.88	190	42
Fluid Loss B	0.50	190	107
Fluid Loss B	1.50	190	70
Fluid Loss A	1.07	400	32
Fluid Loss B	1.50	400	40

Table 7. Performance Comparison of Dispersant A and Dispersant B.

Product	Solution % NaCl	Shear Stress (rpm)							
		600	300	200	100	60	60	6	3
---	18	183	105	82	60	49	41	25	18
Dispersant A	18	127	62	40	19	11	4	0	0
Dispersant B	18	120	57	37	18	10	5	0	0
---	37	105	59	45	31	26	21	16	14
Dispersant A	37	81	44	28	14	8	3	0	0
Dispersant B	37	95	50	31	15	10	5	1	0
	% CaCl ₂								
---	2	227	117	95	70	59	49	25	18
Dispersant A	2	185	92	59	27	15	7	1	0
Dispersant B	2	150	72	46	22	12	6	1	0

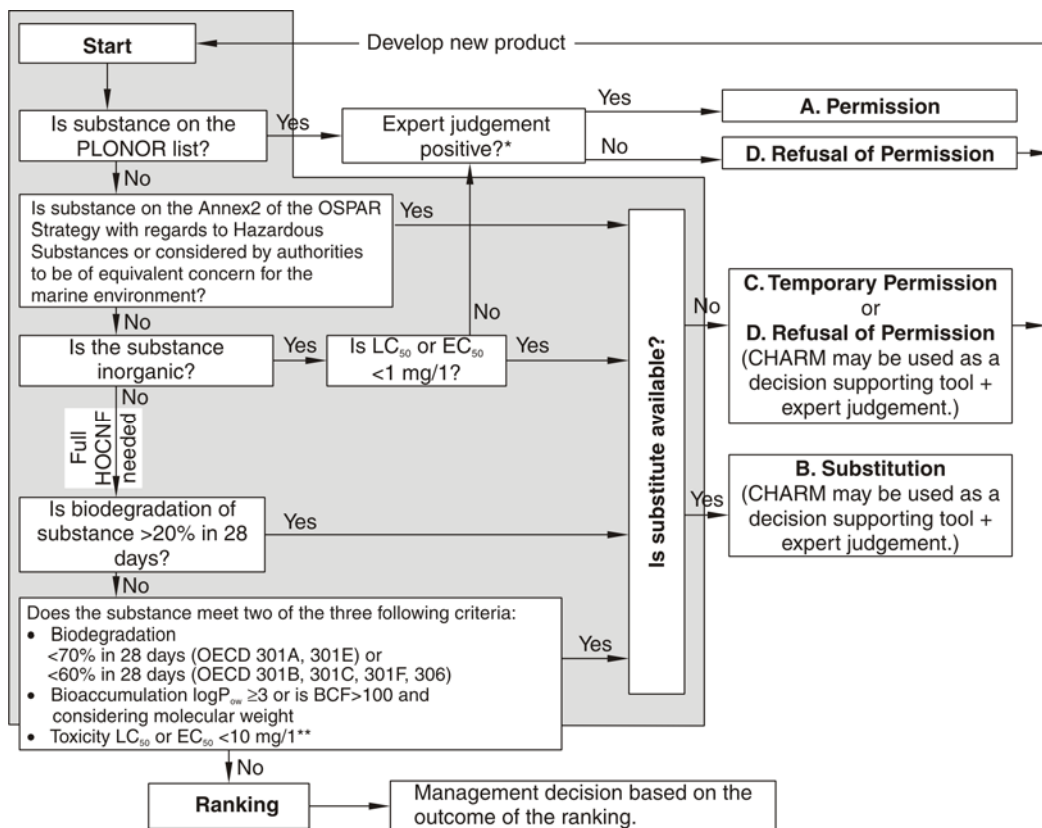


Figure 1. Flowchart used by the HMCS for prescreening.

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