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Development of a Highly Versatile Cement Set Retarder with Global Applicability

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Abstract

Varying regulatory requirements around the world have driven the need for a high-performance cement set retarder that can be used in any geographical location. This paper describes the development of such a retarder. Laboratory studies have shown that this product has superior performance when compared to typical set retarders. The advantages, such as availability, associated with common retarders are retained while eliminating many of the common disadvantages, such as strength development. This set retarder has shown to be useful in applications ranging from low-temperature foam designs to high-temperature densified designs. Performance data and case histories will be discussed.

Introduction

Set retarders for cement are required in many cases to prevent premature setting or to combat gelation tendencies of the cement.[1] These retarders inhibit crystal growth in the cement, thus causing a delay in setting.[2] All retarders act in this fashion and many have similar effective temperature ranges. Despite the similar nature of many retarders, a large variety of retarders are in existence and in use throughout the world. One reason for the abundance of these products is related to differences in environmental standards and regulations among various countries (see Figure 1). This diversity of regulations requires that a multiplicity of retarders (and other additives) be developed and stocked for use in different parts of the world. Consequently, the complexity of dealing with dozens of different materials all designed for the same purpose can lead to logistical problems in terms of managing portfolios and maintaining chemical compliance. As a result, a strong need exists to reduce the number of retarders needed for global operations.

Current Technology

Current retarder technology is largely based on lignins, sugars, or synthetic polymers. Each of these classes has advantages and disadvantages that will be discussed. Table 1 summarizes these advantages and disadvantages.

Lignins

The most common cement retarders are based on lignin chemistry, usually sulfonated lignin. Lignins are structurally very complex but are essentially polyphenols with various hydroxyl groups associated with the structure (see Figure 2). Lignosulfonates are byproducts of the paper industry where the lignin component of wood pulp is detrimental to the mechanical properties of typical paper and is therefore removed via a kraft chemical pulping process that produces the lignosulfonates. The lignosulfonates are water-soluble due to the inclusion of sulfonate groups at various positions of the lignin starting material (see Figure 3). Because they are part of a waste stream, lignosulfonates have wide availability and low cost. However, this aspect of lignosulfonates also lends itself to high variability and poor overall consistency over time.

Lignosulfonates also have a high tendency to disperse cement slurry (which may be beneficial or detrimental) as well as to inhibit the development of compressive strength in the set cement. These compounds are deep red to reddish brown in color and as a powder can cause difficulty in handling due to stickiness and absorbing of water from the atmosphere.

Sugars

Common sugars are the oldest known retarders for cement and also have wide availability and relatively low cost. Sugars are well known to be very erratic and very powerful retarders at temperatures below 200°F. The erratic and inconsistent nature of sugars has led to very limited use of them in cements. Additionally, sugars will simply degrade at temperatures above the boiling point of water (212°F) to become ineffective retarders and often cause side effects in the slurry such as gelation.

Synthetics

The most recent developments in retarder technology are polymers based on acylic acid and/or acrlyamide technologies. The most common monomer is 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) acrylic acid, itaconic acid, or the like. These retarders can have numerous varying properties such as higher temperature range than lignins or sugars, or linear retardation with respect to concentration. They also display less sensitivity to temperature fluctuations and do not cause significant changes in pumping time due to relatively small changes in temperature. The disadvantages of synthetic retarders are high cost and the fact that they are highly hygroscopic. The hygroscopic nature causes numerous problems with handling as the material takes on a sticky/slick syrup-like consistency in very little time when exposed to moisture. This has a tendency to plug transfer lines and cause slip hazards at the warehouse.

New Technology

The current development consists of a new retarder that is non-lignin and non-synthetic but displays many advantageous properties of both. This material is food grade and meets even the most stringent requirements of the North Sea for environmental compliance. This material is a high-performance environmental retarder (HPER) capable of outperforming most of the current technology available, while having wide availability and a highly consistent supply.

Slurry Properties

The HPER has shown many advantageous properties in the cement slurry form. It is an effective cement set retarder to temperatures up to ~220°F and can be extended to >350°F with retarder enhancers. The HPER has a much better response to concentration than lignin retarders, being closer to the linear response desired in synthetic retarders (Figure 4). There is also a very stable effect on pumping time across temperatures such that minor fluctuations in temperature conditions will not have a great impact on the pump time of the slurry (Figure 5). Additionally, most retarders have a strong dispersing effect on the slurry, making them problematic for slurries with high water content, and with foam, etc. This HPER however displays a thickening effect if used alone and can enhance the properties of other additives, such as dispersing agents or fluid-loss agents (Table 2). Many locations should take into account the ability of the slurry to build gel strength rapidly, sometimes referred to as transition time. Slurries with the HPER have shown no adverse impact on transition times even with the ability to impart some added viscosity to the slurry (Table 3).

The HPER imparts advantageous properties on the set cement as well. Lignins and sugars are well known to cause delayed strength development in cement. Tests have shown that the HPER can actually enhance early strengths rather than inhibit strength development (Table 4). This HPER has been tested over a wide range of slurry densities and shows good slurry stability from 8 to 18 lb/gal, including typical water-extended slurries, pozzolanic slurries, foam slurries, slurries with hollow spheres, densified slurries, etc. It does seem to perform better in API-grade cements than in construction-grade cements but is still competent to retard construction-grade cement slurries.

Physical Properties

This new cement retarder displays several advantageous physical properties as well. It is a free-flowing white powder with low dusting tendencies. The hygroscopic nature of the material is very low and does not tend to alter the performance over time due to water absorption (see Table 5). Unlike most synthetic retarders, the new retarder does not become sticky and plug transfer lines, making it easier to handle in bulk.

Case Histories

There have currently been several jobs run with this new HPER. The data from the jobsite has matched very well with testing done in the laboratory. Some of the parameters for these first jobs are listed in Table 6. The slurries are reported to be as easy to mix as a slurry with any other retarder and easier to formulate.

Conclusions

The current development of a high performance environmental retarder has led to a material that has wide availability, excellent consistency, impressive performance, and North Sea acceptability while being cost-competitive with lignin retarders. The HPER shows nearly linear retardation response with concentration rather than the somewhat erratic “S-curve” responses seen in lignins. Strength development is unhindered and sometimes enhanced by this material, contrary to what is seen with most other retarders.

Acknowledgments

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References

1. Smith, D.K., *Cementing*, SPE Monograph, Vol. 4, rev. ed. (1987).
2. Bogue, R.H., *The Chemistry of Portland Cement*, 2nd ed. (1955).

Table 1. Comparison of Retarder Types

Retarder Class	Advantages	Disadvantages
Lignin	Low cost Wide availability Often environmentally exempt	Inconsistent performance High sensitivity with extenders Highly variable composition Hygroscopic
Sugar	Low cost Wide availability	Inconsistent performance High sensitivity with extenders Often ineffective at >200°F
Synthetic	Consistent performance Consistent product Higher temperature range Linear retardation wrt concentration	High cost Hygroscopic

Table 2. Rheological and Fluid Loss Characteristics of the HPER

Slurry No.	Cement Type	Density, lb/gal	Temp., °F	Fluid Loss, %bwc	Dispersant, %bwc	HPER, %bwc	Rheology								API F.L., ccs/30 min
							600	300	200	100	60	30	6	3	
1	Type 1	15.8	80	0.5	1	0	300+	156.5	107	59	38	22	6	3	84
1a	Type 1	15.8	80	0.5	1	0.2	300+	194	133.5	76	50	28	8	5	219
2	Type 1	15.8	180	0.5	1	0	165	94	67	37	24	13	4	3	202
2a	Type 1	15.8	180	0.5	1	0.2	236	136	100	64	47	33	18	15	144
3	Premium	15.8	80	3	—	0	300+	300+	275	152	98	54	13	7	12
3a	Premium	15.8	80	3	—	0.2	300+	300+	264	142.5	85	48	12	6	12
4	Premium	15.8	180	3	—	0	300+	300+	280	159	100	55	14.5	6	16
4a	Premium	15.8	180	3	—	0.2	300+	300+	274	156	93	52	14	6	20
5	Premium	16.4	80	1.5	0.03	0	181	90	62	33	21	12	4	3	124
5a	Premium	16.4	80	1.5	0.03	0.25	172	89	61	33	21	12	5	4	110
5b	Premium	16.4	80	1.5	0.03	0.5	156	79	54	29	18	10	3	2	102

Table 3. Inpact of HPER on Gel Development

Test	Retarder Concentration	%Water	Temp., °F	Pump Time, hr:min	Temp., °F	Static Time, hr:min	"0" Gel Time, min	Transition Time, min
2	.1%HPER	39.4	140	4:59	140/156	3:29	48	24
4	.25%HPER	39.4	206	9:23	206/250	7:53	3	21
9	1.2%HPER + .3% extender	48.26	300	4:27	300	2:57	55	6
9	1.2%HPER + .3% extender	48.26	300	4:27	300	2:00	75	16

Table 4. Compressive Strength Development

Temperature	100°F		140°F		208°F	
	Base	0.1% HPER	Base	0.1% HPER	Base	0.1% HPER
TT	3:13	7:10	1:30	5:30	<1:00	3:00
500 psi	5:05	9:31	3:14	7:58	2:05	5:56
24 hr	2811	2877	3300	3621	2800	4922
48 hr	3566	3893	4114	4382	3198	5693

Table 5. Stability of HPER Over Time in Liquid Form

Test	Amount of HPER	%Water	Temp., °F	Pump Time, hr:min
1	.35 gal High-temp HPER after 17 days	51.6	300	6:01
1A	.35 gal High-temp HPER after 120 days	51.6	300	6:56

Table 6. Summary of First Field Jobs

Location	BHCT, °F	Density, lb/gal	Cement, sk	HPER, %bwc	Pump Time, hr:min	Other Additives
Victoria, TX	185	12.7	520	0.55	4:31	
Victoria, TX	185	16.4	130	0.25	3:31	
Victoria, TX	187	16.4	255	0.1	3:03	
Victoria, TX	207	16.2	820	0.35	4:12	

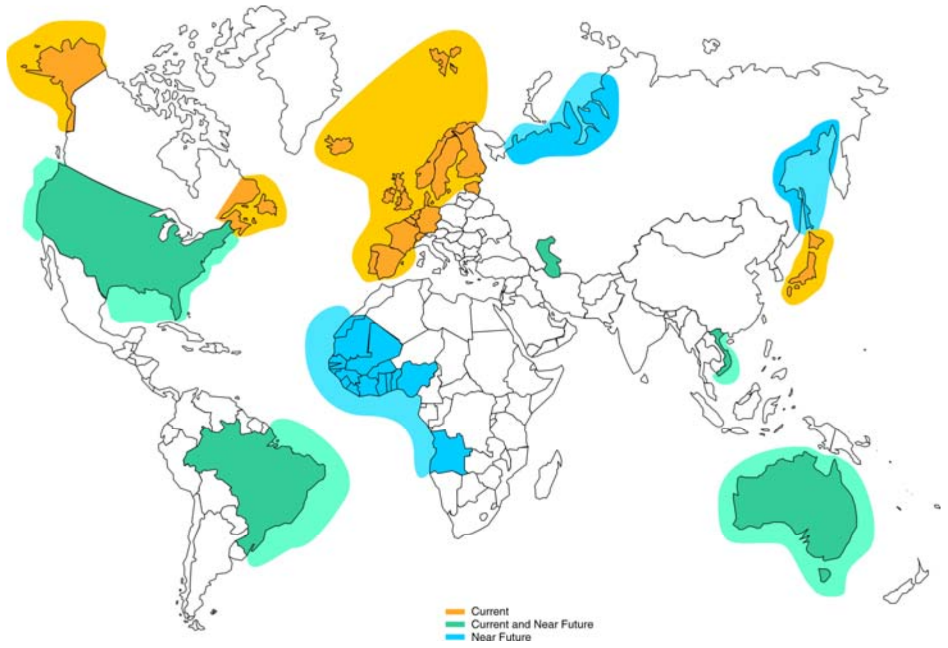

Figure 1. Areas with varying environmental regulations around the globe.

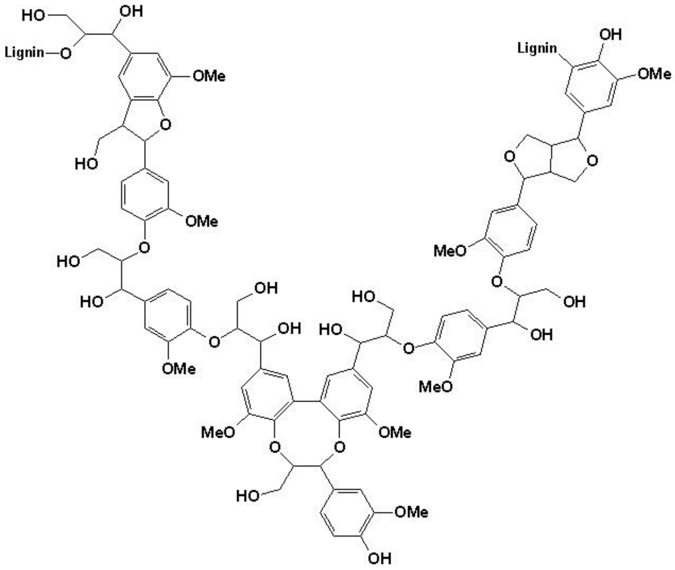

Figure 2. General structural representation of lignin.

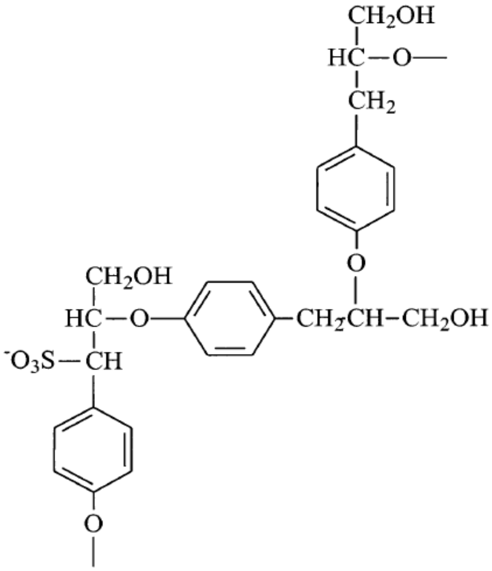

Figure 3. Representation of lignosulfonate structure.

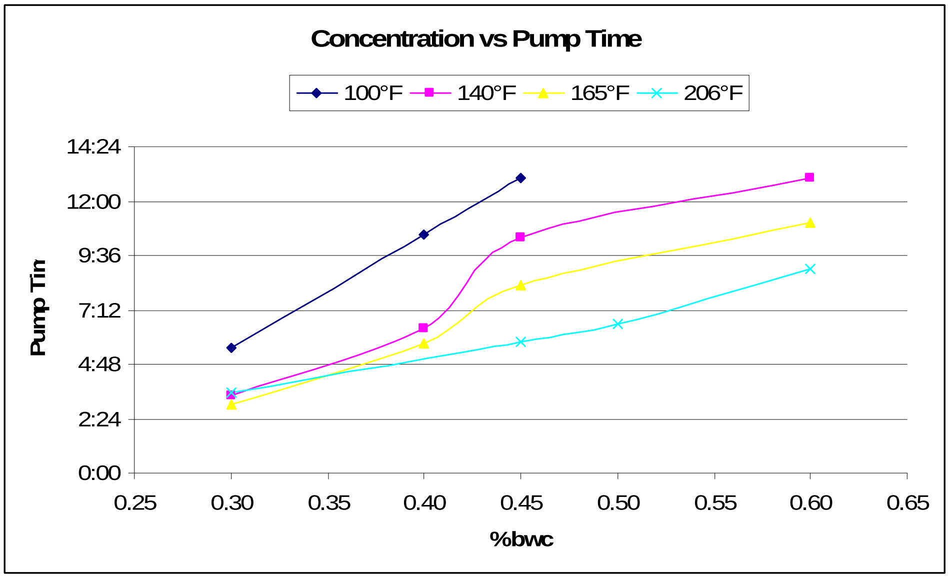

Figure 4. Pump time response to HPER concentration.

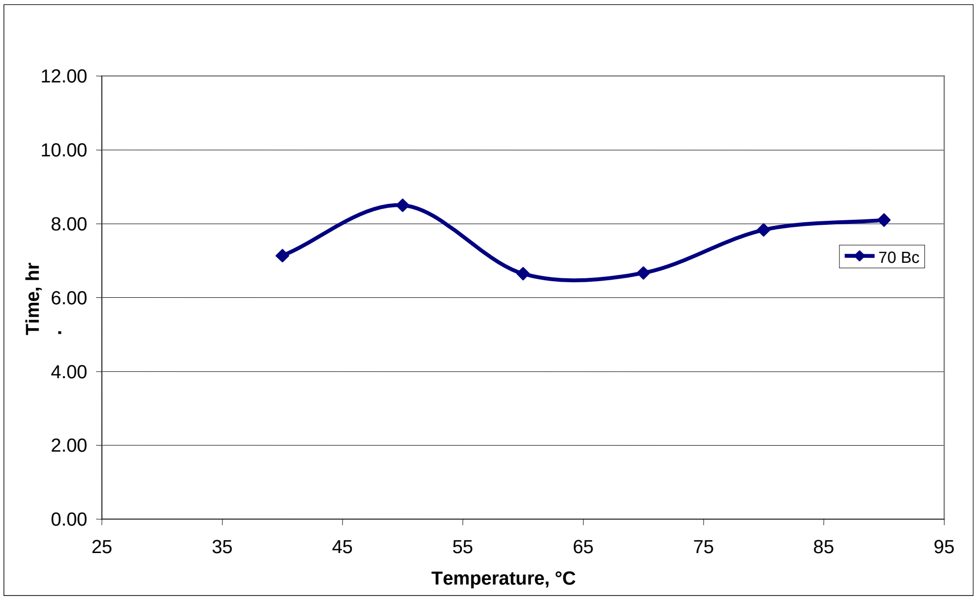

Figure 5. Pump time response to temperature at constant concentration.