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Improved Fluid-Loss Control of Portland Cement Slurry Compositions Using Combination of Modified Biopolymer and Modified Cyclodextrin as Environmentally Acceptable Fluid-Loss Additive

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Abstract

An array of fluid-Loss additives (FLAs) are available for use in hydraulic cement slurries for cementing subterranean zones. Synthetic polymers based on N,N-dimethylacrylamide and sulfonated acrylamide derivative polymers are generally used for high temperature applications. These polymers are typically less environmentally acceptable than biopolymers. Biopolymers used as FLAs sometimes impart high slurry viscosity at ambient temperature, but lead to thinning and settling of the cement slurries at elevated temperatures. Therefore, there is a need for an additive composition that is environmentally acceptable and performs better at elevated temperatures.

This paper describes a novel approach using a combination of a hydrophobically modified (HM) biopolymer and a derivatized cyclodextrin as an environmentally acceptable FLA system. Cyclodextrin (CD) is a cyclic oligosaccharide molecule with a hydrophobic cavity. CD binds selectively to hydrophobic molecules or parts of molecules that fit into the cavity. In aqueous solutions of HM biopolymers, the CD molecules bind primarily to hydrophobic side- or end-groups and not to hydrophilic segments of the backbone. Therefore, the addition of CD provides a unique possibility to specifically decouple the hydrophobic associations caused by the hydrophobic groups grafted onto the polymer backbone, resulting in lower fluid viscosities than if the polymer is used alone. At elevated temperatures, partial dissociation of CD molecules from the polymer can re-establish the hydrophobic associations, thereby increasing slurry viscosity and helping prevent excessive thermal thinning. This concept is tested for reducing high viscosities of the cement slurry imparted by HM biopolymer at ambient temperature. Laboratory studies show that HM biopolymer, when used in combination with derivatized cyclodextrin, help provide optimum slurry rheology and good control of fluid loss, without sacrificing performance at high temperatures.

Introduction

Development of environmentally acceptable cement additives can be challenging. The use of biopolymer is encouraged for this purpose. The primary challenge is to develop environmentally acceptable chemicals that meet the operational criteria and replace synthetic materials presently used.

The selection of FLAs is important for cement placement and zonal isolation. FLAs help prevent water loss from slurries, and thus help prevent cement premature bridging in the annulus. Another frequently useful application of the FLAs is to prevent gas migration in the wellbore annulus, provided that the additive has suitable substituents and charges. The drop in hydrostatic pressure when the cement slurry transforms from liquid state to solid state can provide an opportunity for gas to migrate through the unset cement. Because the FLAs restrict the liquid flow through the cement matrix, they can help prevent the inflow of gas.

The cement slurry containing biopolymers as FLAs can have some undesirable properties, such as (1) increased cement slurry viscosity at surface conditions when used in amounts necessary to provide minimal fluid loss and (2) thermal thinning of the slurry at elevated temperature. Moreover, these FLA additives cannot be used as aqueous solutions because they form highly viscous fluids, even at low polymer concentrations.

This study uses an HM biopolymer (HMHAG) along with derivatized cyclodextrin (CD-1) as an FLA. HM biopolymers in combination with a derivatized cyclodextrine provide cement slurries with excellent fluid-loss control and stable rheologies at elevated temperatures. In general, guar based polymers are used as gelling (viscosifying) agents as they provide viscous fluids with good retention of viscosity, even at higher temperatures. This work makes use of an HM guar gum (HMHAG). The compound HMHAG works very well in terms of controlling fluid loss of the slurry; but, because of hydrophobic molecular association, it also imparts higher viscosities to the cement slurry.

Inhibition of hydrophobic interactions by cyclodextrins is a well-studied concept in paint industries[1]. CD is a cyclic oligosaccharide molecule with a hydrophobic cavity. CD binds selectively to hydrophobic molecules or parts of molecules that fit into the cavity. **Figure 1** presents the schematic diagram of these interactions. In aqueous solutions of HM polymers, the CD molecules bind primarily to hydrophobic side- or end-groups and not to hydrophobic segments of the backbone. Therefore, the addition of CD provides a unique possibility to specifically decouple the association caused by hydrophobic groups grafted to the polymer backbone. The deactivation of hydrophobic associations by CD provides a unique opportunity to reduce the viscosity with little or no dispersant/surfactant.

The same concept for reducing the high slurry viscosities imparted by HM guar gum was used. Thus, HM guar gum was used in combination with hydroxypropyl cyclodextrin to obtain optimum slurry rheology and good control of fluid loss of the cement slurry[1].

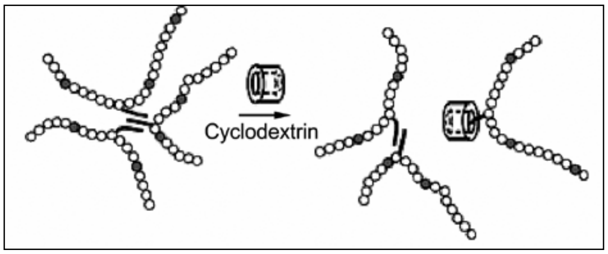

Figure 1: Schematic representation of the disruption of the polymer association following the complex formation between cyclodextrin and polymer hydrophobic groups.

Experimental Methods

All of the cement slurries and fluid-loss measurements were performed according to API Recommended Practice API 10B-2. All slurries were mixed with Class G cement at 15.8 pounds per gallon (lb/gal) density and the slurry composition is specified in the appropriate table headings. Two types of dispersants were used during the course of study. One is an environmentally acceptable dispersant, EAD-8. Another dispersant is a commonly used synthetic cement dispersant D-3. Cement slurries were conditioned at the respective temperatures for 30 minutes in atmospheric consistometers before fluid-loss measurements were performed. The rheology of the cement slurries were taken using a Fann 35 visometer (Fann Instruments) with an F1 spring before and after conditioning. The fluid-loss values are reported as measured values of filtrate volumes collected over 30 minutes and doubled according to API guideline.

Results and Discussion

This study used HMHAG as the primary FLA. Because HMHAG is a low toxicity biopolymer, and CD-1 is also a nontoxic biomolecule, the combination of these two was anticipated to make an environmentally acceptable FLA [2-10]. HMHAG, when used independently, imparts high cement slurry rheology. It is well-known that, depending on the concentration, addition of a surfactant can either increase or decrease the viscosity of a solution of an HM-polymer solution[1]. At high surfactant concentrations, associations between hydrophobic parts of the polymer chains are disrupted. However, this method is unselective and is expected to inhibit all types of hydrophobic interactions (including both interactions from the hydrophobic pendant groups as well as from hydrophobic patches of the main polymer backbone). A much more selective method to disrupt only some types of hydrophobic interactions is offered by the addition of cyclodextrins, a group of cyclic oligosaccharide substances with a hydrophobic cavity in an otherwise hydrophilic molecule. In an aqueous environment, the hydrophobic cavity of the cyclodextrin can host a hydrophobic molecule or a hydrophobic part of a molecule, provided that it fits into the geometry of the cavity. A hydrophobic group of an HM-polymer that has formed a complex with a cyclodextrin molecule does not take part in the thickening mechanism. Hence, it would be possible to tailor the rheology of aqueous solutions and slurries of HM polymers by the addition of cyclodextrin molecules. Conceptually, this mechanism was extended in this study to cement slurries and the experimentation demonstrated that the combination of HMHAG and CD-1 can successfully control fluid loss of cement slurries without sacrificing good cement slurry rheology.

A) Fluid-Loss Control Properties

The compound HMHAG worked to control the fluid loss from the cement slurry in the concentration range 0.3 to 0.4% bwoc (by weight of cement) when used in combination with an environmentally acceptable dispersant at concentration range 0.4 to 0.5 gal/sack of the cement. However, because of hydrophobic association, the rheology of the cement slurry was too high, as shown in **Table 1**. It is important to note that "Rheology"

Table 1: Slurry Composition: Class G cement 15.8 lb/gal, HMHAG 0.4% bwoc, EAD-D8 0.5 gal/sack

rev/min	Rheology at Mix RT (75°F)	Rheology at 170°F
3	58	43
6	65	53
30	109	106
60	149	134
100	195	171
200	293	245
300	300+	300+
API fluid loss (mL/30 min)	48	

When derivatized CD-1 was added to the same slurry at 0.5% bwoc, the rheology of the slurry was lowered, and the slurry remained free-flowing and pumpable due to formation of an inclusion complex of HMHAG and CD-1.

The results showed that CD-1 helps disrupt the hydrophobic association without sacrificing the control of fluid loss, as shown in **Table 2**.

Table 2: Slurry Composition: Class G cement 15.8 lb/gal, CD-1 0.5% bwoc, HMHAG 0.4% bwoc, EAD-D8 0.5 gal/sack

rev/min	Rheology at mix RT (75°F)	Rheology at 170°F
3	12	12
6	21	19
30	64	54
60	102	86
100	144	122
200	228	194
300	269	251
API fluid loss (mL/30 min)	42	

The combination of HMHAG and CD-1 when dry blended worked well to control the fluid loss from the cement slurry even at higher temperatures, such as 190°F. **Table 3** gives the rheology and fluid-loss control of the cement slurry at 190°F. The rheology readings at 190°F indicated that the slurry did not thin down; hence, settling problems may be avoided, even at high temperatures.

Comparisons of the results in Tables 1 through 3 indicate that complexation of CD-1 and hydrophobic groups on the HMHAG could be responsible for the decreased rheologies at room temperature as well as at test temperatures. Tests were also performed by premixing HMHAG and CD-1 in mix water before the addition of cement, similar results were obtained, adding additional support to the assumption.

Table 3: Slurry Composition: Class G cement 15.8 lb/gal, CD-1 0.5% bwoc, HMHAG 0.4% bwoc, EAD-D8 0.5 gal/sack

rev/min	Rheology at mix RT (75°F)	Rheology at 190°F
3	12	11
6	19	19
100	118	110
200	189	164
300	247	213
API fluid loss (mL/30 min)	50	

B) Thickening Time Testing

The combination of HMHAG and CD-1 when used with an environmentally acceptable dispersant, EAD-D8, retarded the slurry. The thickening time test run with the slurry composition (Class G cement, CD-1 0.5% bwoc, HMHAG 0.4% bwoc, and EAD-D8 0.5 gal/sack at a density of 15.8 lb/gal) gave thickening time of 7 hours and 55 minutes at 190°F and 9,000 psi pressure. It should be mentioned that the retardation observed here was not only the effect of CD-1 and HMHAG combination, but also reflected the contribution of the dispersant, which is known to retard the slurry slightly. **Figure 2** depicts the thickening time curve at 190°F and 9,000 psi pressure.

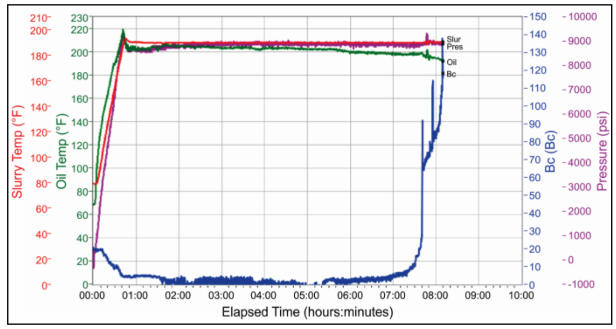

Figure 2: Thickening time graph for the slurry: Class G cement 15.8 lb/gal, CD-1 0.5% bwoc, HMHAG 0.4% bwoc, EAD-D8 0.5 gal/sack

Because β-cyclodextrin is known to retard the cement slurry, there is a possibility that CD-1 was the primary retarder in the cement composition. However, it was not clear whether HMHAG was also functioning as a retarder. To rule out this possibility, another thickening time test was conducted without adding HMHAG, i.e. by adding only CD-1 and EAD-D8 to the slurry. The thickening time for this test was 8 hours and 25 minutes, which indicated that HMHAG was probably not responsible for the retardation.

C) Compressive Strength Development

Based on ultrasonic cement analyzer (UCA) test, the slurry containing the additive combination of HMHAG (0.4% bwoc) and CD-1 (0.5% bwoc) along with the dispersant EAD-D8 powder (1.77% bwoc, equivalent to about 0.5 gal/sack of the liquid additive) developed 1,000 psi in 25.5 hours, and 2,927 psi in 48 hours **(Figure 3)**. The UCA test results suggested that the additives did not significantly affect compressive strength development of the cement, except for an initial retardation. The shorter retardation time observed with thickening time test (7 hours and 55 minutes) as compared to that observed from the UCA tests (21 hours) may be attributed to conditioning effect of the former.

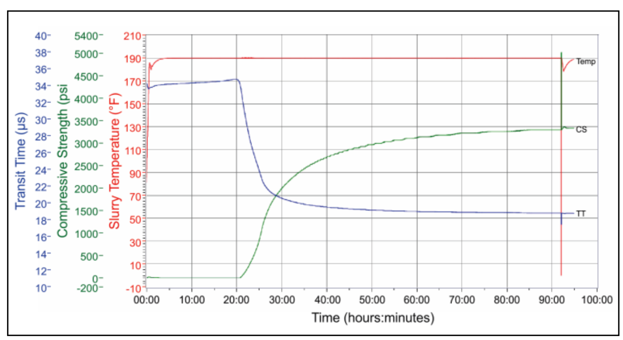

Figure 3: Compressive strength development for the slurry Class G cement 15.8 lb/gal, CD-1 0.5% bwoc, HMHAG 0.4% bwoc, EAD-D8 (powder form) 1.77% bwoc

The compressive strength development of the slurry containing the additive combination of HMHAG (0.4% bwoc) and CD-1 (0.5% bwoc) along with the dispersant D3 (1.0 % bwoc) was also studied. D3 is regularly used in cement formulations as a dispersant and is not known to retard the cement slurry significantly. According to the UCA test, this slurry began developing compressive strength in 14 hours, which compares to 21 hours when EAD-D8 was used as dispersant, indicating that the latter has a stronger retardation effect. As shown in **Figure 4**, the slurry attained 500 psi strength in 16 hours, developed 1,928 psi in 24 hours, and 2,700 psi in 48 hours, suggesting that the additive combination (HMHAG and CD-1) did not significantly affect compressive strength development of the cement.

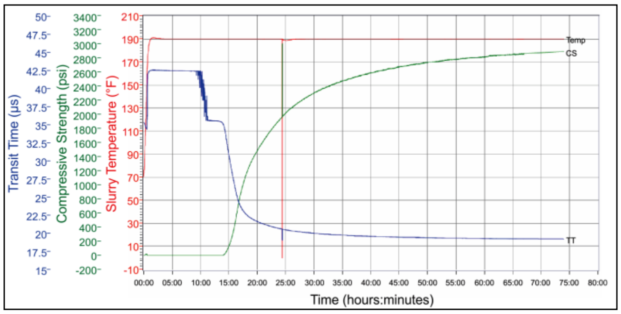

Figure 4: Compressive strength development for the slurry Class G cement 15.8 lb/gal, CD-1 (0.5% bwoc), HMHAG (0.4% bwoc), D3 (1.0% bwoc)

Conclusions

- The biopolymer HMHAG and the derivatized cyclodextrin CD-1 worked synergistically to control fluid loss of cement slurries and can potentially be used as an environmentally acceptable FLA.
- CD-1 helped limit the high slurry viscosities caused by the HMHAG at ambient temperature and provided cement slurries with workable rheology profiles.
- The combination of these two additives introduce some retardation effect to the cement, but did not significantly affect compressive strength development.
- The retardation of cement hydration seems to be primarily attributed to CD-1 instead of HMHAG.
- Using a combination of HMHAG, CD-1, and bio-based dispersant, cement slurry formulations with only biodegradable or biologically originated additives can be designed.

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