AADE-18-FTCE-017

PCE Superplasticizers Used as Dispersants in Oil Well Cementing

Y. Bin, Z. Hu, L. Yuwei, China Oilfield Services Limited (COSL), M. Moumin and J. Plank, Technische Universität München, Germany

Copyright 2018, AADE

This paper was prepared for presentation at the 2018 AADE Fluids Technical Conference and Exhibition held at the Hilton Houston North Hotel, Houston, Texas, April 10-11, 2018. This conference is sponsored by the American Association of Drilling Engineers. The information presented in this paper does not reflect any position, claim or endorsement made or implied by the American Association of Drilling Engineers, their officers or members. Questions concerning the content of this paper should be directed to the individual(s) listed as author(s) of this work.

Abstract

Cementing oil wells requires highly effective dispersants to allow for pumping a cement slurry mixed at low w/c ratio (typically 0.38 – 0.44) over 10 km or more in a very narrow annulus. Furthermore, well temperatures can reach 200 °C or higher which demands high temperature stable polymers.

Since the 1980s, acetone–formaldehyde–sulfite (AFS) polycondensate has become the dominant dispersant in oil well cementing. It is temperature stable and well compatible with other common cement additives such as fluid loss polymers. Up until now, only very limited amounts of PCE superplasticizers are used in oil well cementing, because of the overall good performance of AFS.

At first, the dispersing effectiveness of chemically different PCE polymers (MPEG, APEG and IPEG types) was compared at room temperature and 80 °C by measuring the shear–dependent rheology of cement slurries. It was found that the PCEs (especially the IPEG type) perform vastly superior over AFS, albeit at 80 °C the dosage gap becomes more narrow.

Furthermore, compatibility of the PCEs with lignosulfonate and tartaric acid retarders was studied. It was observed that the dispersing performance of two PCE dispersants was significantly reduced, while one PCE proved to be more robust in the presence of the retarders. Generally, lignosulfonate (LS) was found to impair PCE performance much stronger than tartaric acid (TA). A mechanistic investigation revealed that the negative impact of tartaric acid derives from hindrance of PCE adsorption on cement through competitive adsorption.

Moreover, additional experiments revealed that the PCE polymers substantially improve the water–retention effectiveness of cement fluid loss polymers such as e.g. HEC or AMPS/NNDMA copolymers. This secondary effect can offer huge cost savings relative to total slurry cost.

The results suggest that PCE dispersants are quite sensitive in the presence of retarders, however, specific polymer compositions can provide significant robustness. Furthermore, the results confirm that in the presence of cement fluid loss polymers, the application of PCE polymers can offer substantial advantages in oilwell cementing.

Introduction

The most important purpose of wellbore cementing is zonal isolation. To achieve this goal, different additives are admixed for optimum slurry performance [1].

In general, cement dispersants – in the concrete industry known as superplasticizers - are used to adjust the desired rheological properties of a cement slurry. The two major groups of superplasticizers used in concrete include polycondensates and polycarboxylate ethers (PCEs) [2].

In oil well cementing, however, polycarboxylates are currently only rarely used while the acetone–formaldehyde–sulfite (AFS) dispersant is still dominant [3]. Because of the high effectiveness of PCEs it is surprising that they have not yet found a broader acceptance and application in the oilfield.

Another popular admixture used in cementitious systems is lignosulfonate [4]. In concrete, the major application of lignosulfonate in ready–mix concrete includes the plastification of stiff concrete to enhance its flowability, pourability and workability. Furthermore, lignosulfonates are also known to retard cement hydration [5]. This effect is particularly utilized at high temperatures in oil well cementing [1].

The combination of several admixtures can produce synergistic or antagonistic effects between them [6, 7]. For example, when applying a sodium lignosulfonate retarder together with an AMPS-based fluid loss additive in oil well cement, a synergistic effect resulting in improved fluid loss performance and stronger retardation was observed [8].

The objective of the present study was to analyze the potential of different PCE superplasticizers for application in oil well cement slurries and their effectiveness in the presence of other additives. For this purpose, three different types of PCEs (MPEG, APEG and IPEG type) were synthesized. At first, the dispersing performance of the individual PCEs in oil well cement was investigated. Furthermore, their dispersing capacity was assessed in the presence of lignosulfonate and tartaric acid retarders and silica flour. The experiments were conducted at different temperatures (27 °C and 80 °C) and the results were compared with those obtained from a conventional AFS dispersant. Furthermore, fluid loss measurements were taken from combinations of two different PCE dispersants (MPEG and IPEG) with HEC and an AMPS-based copolymer.

Material and Methods

Oil well cement

For all measurements an API Class G oil well cement according to *American Petroleum Institute* (*API*) specification 10 A was used [9]. Its phase composition, specific density and specific surface area (*Blaine* method) as well as its average particle size (d_{50} value) are listed in **Table 1**.

Table 1: Phase Composition (Q-XRD, *Rietveld*), specific density, specific surface area (*Blaine*) and d_{50} value of the API Class G oil well cement sample used in the study.

Component/ Property	value
C_3S [1] (wt.%)	59.3
C_2S [2] (wt.%)	19.5
C_3A_c [3] (wt.%)	1.7
C_4AF [4] (wt.%)	14.1
Free CaO (wt.%)	<0.3
$CaSO_4 \cdot 2H_2O$ [5] (wt.%)	4.6
$CaSO_4 \cdot 1/2\ H_2O$ [5] (wt.%)	0.2
$CaSO_4$ (wt.%)	0.0
Specific density (kg/L)	3.18
Specific surface area (cm^2/g)	3,058
d_{50} value (µm)	11.0

[1] C_3S: tricalcium silicate ($Ca_3(SiO_4)O$); [2] C_2S: dicalcium silicate (Ca_2SiO_4); [3] C_3A_c: cubic modification of tricalcium aluminate ($Ca_9Al_6O_{18}$); [4] C_4AF: tetra calcium aluminate ferrite ($Ca_4Al_2Fe_2O_{10}$); [5] Measured by thermogravimetry.

Retarder samples

Natural 2R,3R tartaric acid (TA), sodium lignosulfonate (LS), as well as the defoamer were commercial products and used as obtained. The chemical structures of the two retarders are presented in **Figure 1**.

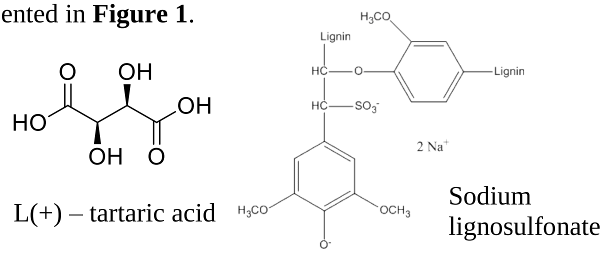

Fig. 1: Chemical structures of the two retarders, L(+)-tartaric acid and sodium lignosulfonate, used in the study.

Fluid loss polymer samples

HEC (hydroxyethyl cellulose) and AMPS-*co*-*N*,*N*- dimethyl acrylamide (AMPS/NNDMA) copolymer were commercial samples. Their chemical structures are presented in **Figure 2**.

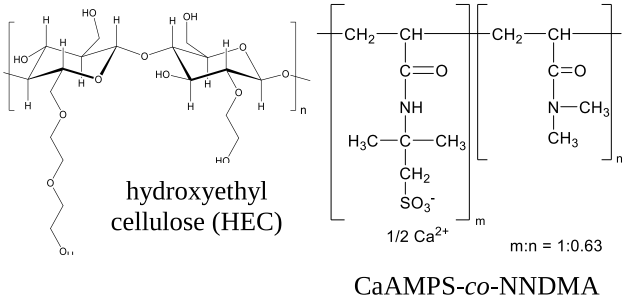

Fig. 2: Chemical structures of the fluid loss additives used in the study.

Polycarboxylate and polycondensate dispersant samples

The three different polycarboxylates (APEG, MPEG and IPEG type) used in the study were synthesized in our laboratory following literature descriptions [10]. The AFS dispersant was a commercial sample which was used as obtained. The chemical structures of all dispersants are shown in Figure 3.

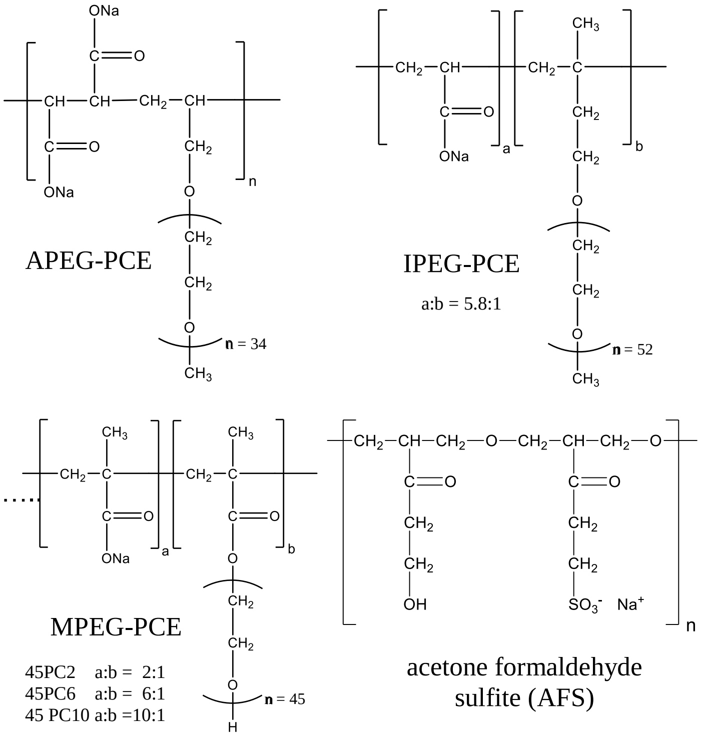

Fig. 3: Chemical structures of the dispersant samples used in the study.

Silica flour

A commercial sample of silica flour containing (wt.%) quartz 97.60, CaO 0.57, MgO 0.18, Al_2O_3 0.17, TiO_2 0.06 (as determined by X-ray fluorescence analysis) and a loss on ignition (LOI) of 1.40 wt.% was used, with a specific surface area (*Blaine* method) of 1,857 cm^2/g, an average particle size (d_{50} value) of 32.7 µm and a specific density of 2.65 kg/L.

Cement slurry composition

The compositions of the cement slurries for which rheology was tested are presented in **Table 2** and **Table 3**. **Table 4** shows the cement slurry composition which was used for the fluid loss measurements. The amount of the API class G cement was 700 g.

Table 2: Composition of the cement slurry (w/c = 0.35) used in the rheological measurements at 27 °C.

Component	Amount (g)	Dosage (% bwoc)
Dispersant	0.35 - 2.8	0.05 - 0.4
Defoamer	0.7	-

Table 3: Formulation of the high temperature cement slurry (w/c = 0.38) used in the rheological measurements at 27 °C and 80 °C.

Component	Amount (g)	Dosage (% bwoc)
Silica flour	245	35
Lignosulfonate	4.2	0.6
Tartaric acid	3.15	0.45
Dispersant	0.7 - 2.1	0.1 - 0.3
Defoamer	0.7	-

Table 4: Formulation of the cement slurry (w/c = 0.44) used for the fluid loss measurements at 27 °C.

Component	Amount (g)	Dosage (% bwoc)
AMPS/NNDMA or HEC	3.50 or 2.80	0.5 or 0.4
Dispersant	0.7 – 2.8	0.1 – 0.4

Slurry preparation

All cement slurries were prepared in accordance with the procedures set forth in *Recommended Practice for Testing Well Cements, API Recommended Practice 10B-2* [11].

Rheological measurements

A *Couette*-type coaxial cylinder rotational viscometer was used for the rheological measurements of the cement slurries. Dial readings were taken every 10 seconds and the rotational speed was changed in the following sequence: 3 - 6 - 100 - 200 - 300 - 200 - 100 - 6 - 3 - 600 rpm. The dial readings were converted into lbs/100 ft^2 units by multiplying them with the factor 1.065 and the torsion spring factor F=1.

Identifying specific additive-additive interactions

In order to determine which additive is responsible for the reduced performance of the dispersants, experiments were conducted using slurries where one component was removed from the slurry and the rheology was then recorded. For those measurements only the PCE sample which had proven to be most effective, namely polymer 52IPEG5.8, was tested at a dosage of 0.1 % bwoc. As a comparison, the commercial AFS polycondensate sample was also evaluated at a dosage of 0.4 % bwoc. The amounts of cement, silica flour, the w/c ratio and the defoamer concentration were kept constant in all slurry formulations (Table 3).

Adsorption of PCE in presence of tartaric acid

The adsorbed amount of PCE was determined from the difference of the PCE concentration in the pore solution of the cement slurry recorded in the absence and presence of tartaric acid. The cement pore solution was obtained by centrifugation. PCE sample 52IPEG5.8 was used as dispersant. Quantification of the adsorbed amounts of PCE was achieved by removing tartaric acid from the cement pore solution via centrifugation using an Amicon® Ultra-4 Centrifugal Filter Device (3 000 MWCO - Molecular weight cutoff). This filter allows tartaric acid to pass through the pores while the large molecule of PCE is retained. The amount of non-adsorbed PCE was assessed via Total Organic Carbon (TOC) content on a High TOC II apparatus (Elementar, Hanau/Germany) equipped with a CO_2 detector.

Fluid loss measurements

Fluid loss measurements were conducted at a pressure of 70 bar N_2 at 27 °C using a 500 mL HP/HT filter press applying the cement slurry which is presented in Table 4.

Results and discussion

PCE effectiveness at room temperature

The rheological measurements which are summarized in **Table 5** revealed that in neat cement slurries all polycarboxylate dispersants (2-6) are superior over the commercial AFS dispersant (7).

The results at the shear rate of 200 rpm show that the IPEG PCE (6) exhibits the best performance followed by the MPEG PCE sample 45PC6 (3). Among the MPEG PCEs (2-4), the strongest effect was observed from 45PC6 (3), whose performance is almost comparable to that of 52IPEG5.8 (6). The dispersant 45PC2 (2) exhibited the least effect of all PCE samples studied. Furthermore, the APEG PCE (5) required twice the dosage of 52IPEG5.8 (6) to achieve comparable slurry rheology. Of AFS (7), about four times as much is needed to reach the same rheological values as for the PCE sample.

PCE performances at high temperature

High temperature cement slurries were prepared by adding silica flour and a combination of two retarders (LS and TA) to accommodate for the high temperature conditions. The composition of the cement slurry used here was shown before in **Table 3**. **Table 6** summarizes the results of the rheological measurements obtained at 27 °C and 80 °C, respectively.

The best dispersing performance again was achieved by PCE sample 52IPEG5.8 (6), at both 27 °C and at 80 °C. However, here much higher dosages were required than in the neat cement slurry without silica flour and retarders. Apparently, in the presence of silica flour and the two retarders, the performance of the PCE dispersants (3,6) was severely impacted. All PCE samples (3,6), but also the AFS dispersant (7) show a significant decrease in performance, with some producing no dispersing effect at all anymore. For example, at 27 °C such total loss in performance was observed even for PCE sample 45PC6 (3) which presents a standard product used in large quantities by the concrete industry. This effect is most pronounced at 27 °C and less noticeable at 80 °C, thus suggesting that the PCE dispersants (3,6) become more effective at higher temperature.

Table 5: Rheology of the neat cement slurry at 27 °C treated with different PCE dispersants and AFS.

	Dispersant	Dosage (% bwoc)	Shear stress (lbs/100 ft^2) at shear rate (rpm)					
			3	**6**	**100**	**200**	**300**	**600**
(1)	**Blank**	0.0	23	34	156	194	228	> 300
(2)	**MPEG-45PC2**	0.1	17	22	63	96	128	229
		0.2	5	6	31	59	86	165
(3)	**MPEG-45PC6**	0.05	18	22	56	83	113	199
		0.075	7	8	29	53	79	157
		0.1	1	2	14	29	47	107
(4)	**MPEG-45PC10**	0.05	21	27	71	103	128	198
		0.075	17	20	42	63	85	146
		0.1	6	7	26	45	66	126
(5)	**APEG**	0.1	11	12	38	62	89	164
		0.2	1	1	13	31	47	110
(6)	**52IPEG5.8**	0.05	12	14	44	68	93	173
		0.075	3	4	24	48	72	141
		0.1	1	2	14	30	54	105
(7)	**AFS**	0.1	22	33	111	144	174	257
		0.2	18	24	66	93	116	195
		0.3	5	6	27	49	76	150
		0.4	1	2	20	42	68	141

Of all dispersants tested, AFS (7) was least affected by the presence of the retarders and silica flour. For example, at 0.3 wt.% addition of AFS (7), similar rheology than from 0.3 wt.% of 52IPEG5.8 (6) was achieved. Considering the lower cost of AFS (7) compared to the PCE (3,6), this finding explains why so far PCEs encountered difficulties to become accepted in the oilfield. The result also confirms that the AFS dispersant (7) is more robust in the presence of other admixtures such as retarders.

To summarize, the performance of all PCE dispersants (3,6) decreases significantly in the presence of silica flour and the two retarders, with IPEG PCE sample 52IPEG5.8 (6) being least affected. In order to determine which specific additive (LS, TA or silica flour) was responsible for this negative effect, additional tests were conducted whereby always one component was selectively removed from the slurry while the others were still kept.

Table 6: Rheological properties of the cement slurry holding 35 % bwoc silica flour, and two retarders, measured at 27 °C and 80 °C.

	Dispersant	T (°C)	Dosage (% bwoc)	Shear stress (lbs/100ft^2) at shear rate (rpm)					
				3	**6**	**100**	**200**	**300**	**600**
(1)	**Blank**	27	0.0	15	21	112	206	> 300	> 300
		80	0.0	7	13	78	149	218	> 300
(3)	**MPEG-45PC6**	27	0.1	19	21	118	219	> 300	> 300
			0.2	17	21	120	232	> 300	> 300
			0.3	10	12	104	206	> 300	> 300
		80	0.1	10	12	67	130	194	> 300
			0.2	4	6	59	121	181	> 300
(6)	**52IPEG5.8**	27	0.1	14	19	125	238	> 300	> 300
			0.2	3	6	104	225	> 300	> 300
			0.3	2	3	72	179	> 300	> 300
		80	0.1	8	11	51	94	140	255
			0.2	2	4	40	81	125	213
(7)	**AFS**	27	0.1	15	20	106	189	271	> 300
			0.2	16	21	106	187	271	> 300
			0.3	17	21	110	201	276	> 300
		80	0.1	10	12	73	139	202	> 300
			0.2	7	9	58	110	170	> 300
			0.3	9	11	61	119	184	> 300

Identifying specific additive-additive interactions

To gain insight into the additive-additive interactions underlying the negative impact on PCEs, measurements were conducted on cement slurries containing either 52IPEG5.8 (6) (dosage 0.1 % bwoc) or AFS (7) (0.4 % bwoc) as dispersant, and at varying dosages of the retarders and silica flour. The results of these measurements taken at 27 °C and 80 °C are summarized in **Tables 7 and 8**.

Effect of retarders on PCE and AFS at 27 °C

The results displayed in **Table 7** obtained at 27 °C clearly demonstrate that the performance of the PCE polymer is strongly impeded by both retarders. However, the negative effect of lignosulfonate is much more pronounced than that from tartaric acid.

This negative interaction can be explained by competitive adsorption between the PCE and the lignosulfonate, whereby the lignosulfonate prevents the PCE from adsorbing on cement in an amount which is sufficient to provide a strong dispersing effect. Consequently, such combination produces poor results with respect to slurry rheology.

Table 7: Rheology of the high temperature cement slurry in the presence or absence of individual retarders and silica flour, measured at 27 °C.

Component	Shear stress (lbs/100 ft^2) at shear rate (rpm)					
	3	**6**	**100**	**200**	**300**	**600**
52IPEG5.8+LS+TA+ silica flour	14	19	125	238	> 300	> 300
- w/o LS	1	1	50	135	250	> 300
- w/o TA	13	19	99	179	256	> 300
- w/o LS+TA	6	7	54	113	175	> 300
- w/o silica flour	9	10	28	49	72	132
AFS+LS+TA+silica flour	17	23	121	224	> 300	> 300
- w/o LS	12	17	108	204	306	> 300
- w/o TA	7	11	94	178	259	> 300
- w/o LS+TA	10	13	86	166	244	> 300
- w/o silica flour	10	11	27	46	66	117

w/o = without

For the AFS dispersant, both retarders imply a weaker effect on its dispersing performance, i.e. in their presence, rheology of the AFS is higher than in their absence, but the difference is less than in case of the PCE. Here, the negative contribution from tartaric acid is more pronounced than that from lignosulfonate. However, altogether the effect of both retarders on AFS is not as severe as it is for the polymer 52IPEG5.8.

The data suggests that AFS and PCE are both negatively affected by the presence of the retarders, but AFS presents the more robust dispersant in such combinations.

Effect of retarders and silica flour on dispersants at 80 °C

The results obtained at 80 °C displayed in **Table 8** show that at this temperature, for the PCE polymer again lignosulfonate has an extremely strong negative influence on its dispersing performance, while tartaric acid actually provides a synergistic effect by lowering the slurry rheology at 80 °C.

A different behavior was observed for the AFS dispersant. There, lignosulfonate has no negative effect on the dispersing power of AFS. Thus, in its absence, the rheology of the AFS slurry remains essentially unchanged. Opposite to this, tartaric acid exerts a slightly negative impact on the dispersing ability of AFS, as the rheology becomes lower in the absence of this retarder.

However, at both temperatures, 27 °C and 80 °C, silica flour implies by far the strongest effect on slurry rheology, independent of the type of dispersant used. In its absence, slurry rheology becomes very low, thus signifying that its high surface area consumes a large amount of dispersant.

Table 8: Rheology of the high temperature cement slurry in the presence or absence of individual retarders and silica flour, measured at 80 °C.

Component	Shear stress (lbs/100 ft^2) at shear rate (rpm)					
	3	**6**	**100**	**200**	**300**	**600**
52IPEG5.8+LS+TA+ silica flour	8	11	51	94	140	255
- w/o LS	1	1	5	12	29	50
- w/o TA	16	21	79	128	178	> 300
- w/o LS+TA	26	33	91	130	174	307
- w/o silica flour	4	5	13	23	31	71
AFS+LS+TA, silica flour	10	13	67	127	190	> 300
- w/o LS	10	15	75	133	192	> 300
- w/o TA	4	6	50	97	150	284
- w/o LS+TA	11	14	61	119	178	> 300
- w/o silica flour	4	5	13	23	32	71

w/o = without

Mechanistic investigation on competitive adsorption dispersant - retarder

To check whether a competitive adsorption between the PCE and tartaric acid was responsible for the antagonistic interaction between the retarder and the dispersant, the concentration of the PCE in the cement pore solution of the slurry was determined before and after addition of tartaric acid. As PCE sample, polymer 52IPEG5.8 was used. The results are presented in **Table 9**.

Table 9: Concentration of PCE polymer 52IPEG5.8 in cement pore solution, in the presence and absence of tartaric acid at different temperatures, measured by TOC.

System	PCE amount (mg/L)	
	27 °C	**80 °C**
PCE solution	2,632	2,632
PCE + cement	830	620
PCE + cement + TA	1,519	1,050

In the initial PCE solution, 2,632 mg/L of the polymer corresponding to a dosage of 0.1 % bwoc were present. Addition of cement removed 68 % of this amount via adsorption on cement, with the remaining concentration of PCE being 830 mg/L. Addition of tartaric acid to the cement slurry holding PCE produces a PCE concentration in the filtrate of 1,519 mg/L, consequently PCE adsorption is reduced from previous 68 % to only 42 %. Apparently, the presence of tartaric acid in the slurry leads to a partial displacement of the PCE from the surface of cement, as is characteristic for competitive adsorption between two additives.

At 80 °C, the adsorption of the PCE is stronger at 79 % of initial dosage and only 620 mg/L of PCE remain in the filtrate. After addition of tartaric acid, PCE adsorption again drops, but at 80 °C to 60 % only vs. 42 % at 27 °C. Obviously, at higher temperature the PCE polymer exhibits a stronger affinity to the positively charged surface sites of cement hydrates which renders it more robust in the presence of tartaric acid retarder.

Fluid loss performance of AMPS/NNDMA copolymer in the presence of AFS and PCE at 27 °C

In order to investigate the influence of different dispersants on the fluid loss control performance of AMPS/NNDMA, fluid loss measurements were conducted with either a polycondensate (AFS) or a PCE sample (52IPEG5.8 or 45PC6) at w/c = 0.44 and 27 °C.

Table 10: API fluid loss and thickness of the cement filter cake of the cement slurries (w/c = 0.44) holding 0.5 % bwoc of AMPS/NNDMA fluid loss additive and additional amounts of AFS, MPEG- or IPEG-PCE dispersants, measured at 27 °C.

Slurry	**Dosage (% bwoc)**	**Fluid Loss (mL/30min)**	**Filter cake (cm)**
Blank (0.5 % AMPS/NNDMA)	0	48	2.0
+ MPEG-45PC6	0.1	30	1.3
	0.2	30	1.1
+ 52IPEG5.8	0.1	30	1.1
	0.2	28	1.0
+ AFS	0.2	76	3.0
	0.4	80	3.0

The results confirm that the combination of AMPS/NNDMA with a dispersant decreases or increases the fluid loss volume (**Table 10**). In the presence of PCE dispersants (45PC6 and 52IPEG5.8), the fluid loss volume decreases from 48 (AMPS/NNDMA only) to 30 mL/30 min (PCE dosage of 0.1 % and 0.2 % bwoc) while in combination with AFS the fluid loss increases from 48 (AMPS/NNDMA) to 76 mL/30 min at 0.2 % addition.

The data suggests that the PCEs exhibit a strong positive influence on the fluid loss performance of AMPS/NNDMA. A “fake” low fluid loss because of slurry sedimentation was ruled out for all slurries because in all measurements, no thick filter cake was detected (**Table 10**).

Fluid loss performance of HEC in the presence of AFS and PCE at 27 °C

Furthermore, the influence of different dispersants on the fluid loss control performance of HEC was determined by measuring the fluid loss volumes with AFS and two different PCE samples (52IPEG5.8 and 45PC6) in the cement slurry (w/c = 0.44; at 27 °C).

The results confirm that the combination of HEC with any dispersant decreases the fluid loss volume (**Table 11**). The combination with AFS decreases the fluid loss from 247 mL (HEC only) to 200 mL/30 min at 0.2 % addition. In comparison, the effect of the PCE samples is much more pronounced than that from AFS. The fluid loss volume decreases to the value of 30 mL/30 min at a dosage of 0.2 % bwoc PCE (for 45PC6 as well as 52IPEG5.8). Because of the thin filter cakes, slurry sedimentation can be excluded (**Table 11**).

Table 11: API fluid loss and thickness of the cement filter cake of the cement slurries (w/c = 0.44) holding 0.4 % bwoc of HEC and additional amounts of AFS, MPEG- or IPEG-PCE dispersants, measured at 27 °C.

Slurry	**Dosage (% bwoc)**	**Fluid Loss (mL/30min)**	**Filter Cake (cm)**
Blank (0.4 % HEC)	0	247*	10.5
+ MPEG-45PC6	0.1	64	3.3
	0.2	30	0.6
+ 52IPEG5.8	0.1	50	2.4
	0.2	30	0.7
+ AFS	0.2	200	8.5
	0.4	48	1.5

* = calculated values due to complete dehydration of cement slurry

Conclusions

In neat oil well cement slurries, PCE polymers exhibit a very strong dispersing effect compared to AFS dispersant. The strongest dispersing performance is achieved by the IPEG PCE sample 52IPEG5.8.

However, in the presence of retarders the performance of the PCE dispersants is significantly perturbed. The effect is dependent on the individual structure of the PCE polymer. For example, MPEG-PCE sample 45PC6 loses its dispersing capacity completely, while others (e.g. IPEG PCE sample 52IPEG5.8) show a less pronounced decrease, comparable to that for AFS. Moreover, the effect of the retarders is strongly temperature dependent. It decreases at higher temperatures. lignosulfonate always affects PCEs more negatively than tartaric acid which has only a slight effect on AFS while lignosulfonate does not affect AFS at all. In comparison, silica flour was found to affect PCE performance even much more negatively than the retarders. A mechanistic investigation revealed that between the IPEG PCE and tartaric acid a competitive adsorption occurs.

The study demonstrates that the AFS dispersant is more robust in combination with retarders, while the PCEs are more sensitive.

The fluid loss additives AMPS/NNDMA and HEC used in the study show an improved performance when combined with PCEs. Apparently, PCEs can be used succesfully in oil well cement to improve the fluid loss performance of HEC and AMPS/NNDMA copolymers.

Nomenclature

45PC2	*polyarboxylate dispersant (MPEG-type), molar ratio of methacrylic acid to MPEG methacrylate is 2:1, side chain consists of 45 ethylene oxid units*
45PC6	*polyarboxylate dispersant (MPEG-type), molar ratio of methacrylic acid to MPEG methacrylate is 6:1, side chain consists of 45 ethylene oxid units*
45PC10	*polyarboxylate dispersant (MPEG-type), molar ratio of methacrylic acid to MPEG methacrylate is 10:1, side chain consists of 45 ethylene oxid units*
52IPEG5.8	*polycarboxylate dispersant (IPEG-type), molar ratio of acrylic acid to IPEG macromonomer is 5.8:1, side chain consists of 52 ethylene oxid units*
AFS	*acetone-formaldyhyde-sulfite, polycondensate dispersant*
Al_2O_3	*aluminium oxide*
AMPS	*2-Acrylamido-2-methylpropane sulfonic acid*
APEG	*ω-allyl poly(ethylene glycol), polycarboxylate dispersant*
API	*American Petroleum Institute*
C_2S	*dicalcium silicate* (Ca_2SiO_4)
C_3A_c	*cubic modification of tricalcium aluminate* ($Ca_9Al_6O_{18}$)
C_3S	*tricalcium silicate* ($Ca_3(SiO_4)O$)
C_4AF	*tetra calcium aluminate ferrite* ($Ca_4Al_2Fe_2O_{10}$)
CaO	*calcium oxide*
$CaSO_4$	*anhydrite gypsum*
$CaSO_4\cdot$ ½ H_20	*hemihydrate gypsum*
$CaSO_4\cdot$ $2\,H_2O$	*dihydrate gypsum*
CO_2	*carbon dioxide*
HEC	*hydroxyethyl cellulose, fluid loss polymer*
IPEG	*ω-isobutenyl poly(ethylene glycol),polycarboxylate dispersant*
LS	*lignosulfonate, retarder*
MgO	*magnesium oxide*
MPEG	*ω-methoxy poly(ethylene glycol), polycarboxylate dispersant*
MWCO	*molecular weight cutoff*
N_2	*nitrogen*
NNDMA	*N,N- dimethyl acrylamide copolymer*
PCE	*polycarboxylate ether superplasticizer*
TA	*tartaric acid, retarder*
TiO_2	*titanium dioxide*
TOC	*total organic carbon*
wt.%	*weight percent*

fluid loss polymer
- AMPS/NNDMA
- HEC

polycarboxylate ether superplasticizer
- APEG
- IPEG-type: 52 IPEG 5.8
- MPEG-type: 45PC2, 45 PC6, 45 PC10

polycondensate dispersant
- AFS

retarders
- LS
- TA

References

1. Nelson, E. B. Well Cementing; Schlumberger Dowell: Sugar Land, TX, 2006.
2. Plank, J., Sakai, E., Miao, C. W., Yu, C., Hong J. X., ”Chemical Admixtures – Chemistry, Applications and Their Impact on Concrete Microstructure and Durability’’, Cem. Concr. Res. 78, 81-99, 2015.
3. Smith, D. K., Cementing (2nd Ed.), Society of Petroleum Engineers, SPE Monograph: New York, 1990.
4. Ramachandran, V. S., Concrete Admixtures Handbook, 2nd Ed. Noyes Publications, Park Ridge, 1995.
5. Myrvold, B. O., “Adsorption of lignosulfonate on cement and the hydration products of cements”, Proceedings 8th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, SP-239-19, Farmington Hills, 2006, pp. 285-296.

6. Plank, J., Winter, C., “Competitive Adsorption between superplasticizer and retarder molecules on mineral binder surface", Cem. Concr. Res. 38, 599-605, 2008.
7. Plank, J., Recalde Lummer, N., Dugonjic-Bilic, F., ”Competitive Adsorption Between an AMPS®-Based Fluid Loss Polymer and Welan Gum Biopolymer in Oil Well Cement’’, J. Appl. Polym. Sci. 116, 2913, 2010.
8. Plank, J., Tiemayer, C., Bülichen, D.; Lummer, N. R., ”A Review of Synergistic an Antagonistic Effects Between Oil Well Cement Additives’’; SPE Symposium on Oilfield Chemistry, The Woodlands, Texas, USA, 8.-10. April 2016, SPE paper 164103.
9. American Petroleum Institute API Specification 10A; 24th Ed.; American Petroleum Institute: Washington, 2010.
10. Lange, A.; Hirata, T.; Plank, J., “Influence of the HLB Value of Polycarboxylate Superplasticizers on the Flow Behavior of Mortar and Concrete”, Cem. Concr. Res. 60, 45-50, 2014.
11. American Petroleum Institute API Specification 10B-2; 22nd Ed.; American Petroleum Institute: Washington, 2005.