

Influence of dispersant structure and mixing speed on concrete slump retention

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Received 5 April 2004; accepted 18 April 2005

Abstract

The relationship between rate of dispersant depletion from the aqueous phase and concrete slump retention was investigated by varying polycarboxylate dispersant structure and mixing speed. The influence of dispersant structure on the rate of slump loss was determined by testing two polycarboxylate-polyether dispersants that differed in charge density. The influence of mixing rate on slump loss was determined by changing mixer rotation speed. The rate of dispersant depletion was influenced by dispersant structure and mixing speed. A higher rate of dispersant depletion was observed at higher mixing speed and with a polymer of higher charge density. In comparing the different mixing procedures, a good correlation was found between slump value and the number of drum revolutions, while a poor correlation was found between slump value and time. Concrete slump retention was influenced by the rate of dispersant depletion and the rate of dispersant depletion was influenced by dispersant structure and mixing speed.

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Keywords: Concrete; Polycarboxylate dispersant; Slump retention

1. Introduction

Cement dispersants based on lignosulfonates were discovered almost 70 years ago, and the first generation of superplasticizers was commercialized about 35 years ago [1,2]. Interested readers are referred to a general review of superplasticizers, rheology testing and the mechanism of dispersant performance [3]. The first generation of superplasticizers was based on sulfonated naphthalene formaldehyde condensates or sulfonated melamine formaldehyde condensates. These dispersants are polymers based on a single repeating unit, which did not allow for much variation of the molecular architecture. A new generation of superplasticizers, based on polycarboxylate polymers with pendant polyether molecules, was discovered over 20 years ago, but they have been widely used in North America for less than 10 years [4]. Polycarboxylate dispersants are

based on two or more structural units that provide for more diversity in possible molecular structures. For example, the relative abundance of anionic units to polyether units can be varied, the molecular weight of the polyether molecule can be varied and the molecular weight of the polycarboxylate main chain can also be adjusted to create polymers with different performance characteristics.

A significant amount of research has been devoted toward increasing the understanding of cement–dispersant interactions and the mechanisms behind dispersant performance [5–15]. Factors that can influence dispersant performance have been studied, including those situations where dispersant performance is less than expected. Cement chemistry, temperature, soluble alkali sulfates, dispersant chemistry and timing of dispersant addition have been shown by the referenced authors to influence dispersant performance. Understanding the conformation of adsorbed dispersant molecules on the surface of cement particles remains an unexplored area that may further advance the understanding of the dispersion process [16–18]. It is recognized that adsorption of molecules onto a particle surface

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is an important phenomenon contributing to the dispersion process [9,11,13]. On the other hand, the availability of dispersant molecules to bind over time has been suggested as an important factor behind maintaining workability [9].

This paper reports on studies of the influence of dispersant structure and mixing speed on the rate of dispersant depletion from the aqueous phase and on concrete slump retention. The ionic composition of the concrete aqueous phase, extent of cement hydration and changes in cement surface area over time were also measured to determine if these variables influenced concrete slump retention.

2. Experimental details

2.1. Materials and mixture proportions

An ASTM C 150 Type I/II portland cement having a Blaine fineness of 412 m²/kg was used for all concrete mixtures and the chemical characteristics are shown in Table 1. Included in Table 1 is an analysis of the calcium sulfate form as measured using a method based on thermogravimetry [19]. Coarse aggregate consisted of angular limestone having a nominal maximum size of 25 mm, a relative density of 2.80 and absorption of 0.72%. Fine aggregate consisted of natural quartz sand with a fineness modulus of 2.89, a relative density of 2.60, and an absorption value of 1.60%.

Two commercially available polycarboxylate cement dispersants were tested in this study. PC-1 and PC-2 dispersants are single component copolymers of methacrylic acid and methoxy polyethylene glycol methacrylate. PC-1 dispersant had a relatively high charge density and low side

chain graft density ratio of 4:1. PC-2 dispersant had a relatively low charge density and high side chain graft density ratio of 2:1. The dispersants were partially neutralized with sodium hydroxide.

Concrete mixture proportions were established using the guidelines set forth in ACI 211 [20] and were based on a nominal 356 kg/m³ cement content. Dispersant dosages were 0.2% polymer by cement weight. A commercially available polyether defoamer was added to minimize air contents and prevent changes in air content with mixing time from influencing slump values. Trial mixtures were prepared using each dispersant, making mixture proportion adjustments with regards to water and aggregate contents, in order to ensure proper yielding of the batch. For mixtures containing dispersant, proportions were adjusted using the sand–aggregate ratio (by volume) to take into account a high level of water reduction. Table 2 summarizes mixture proportions and plastic property test results.

2.2. Equipment and apparatus

All concrete mixtures were prepared in an electric powered rotating drum mixer with 6 cubic foot nominal capacity. Drum rotation rate was adjusted to achieve 4 rpm for slow speed mixing and 18 rpm for high speed mixing. Drum rotation rates were confirmed for both low speed and high speed mixing by counting drum rotations for a timed interval.

Pressure filtration (Fig. 1) was used to extract aqueous phase from mortar samples screened from concrete. The apparatus consisted of two stainless steel filtration funnels connected to a high-pressure nitrogen gas cylinder using 3-way stopcocks and reinforced PVC tubing. By properly configuring the 3-way valve, each filtration unit could be independently operated to process mortar samples spaced 5 min apart. The filter media at the base of the pressure funnel was a 0.2 µm nylon membrane. Aqueous phase was collected in a 30-ml plastic bottle and sealed.

A proprietary gel permeation chromatography (GPC) method was used to analyze aqueous phase samples for the amount of polycarboxylate dispersant present. The GPC method was run using a Waters chromatography system with an evaporative laser light-scattering (ELSD) detector manufactured by Alltech. The ELSD detector is a mass detector that works by evaporation of the mobile phase in a heated drift tube forming nonvolatile particles that scatter laser light and generate the detector response. The quantification of PC-2 dispersant in aqueous phase was determined from a calibration curve. The calibration curve was generated from analysis of 5 known concentrations of PC-2 dispersant and corresponding peak area response. A linear regression algorithm was applied to the data and the resulting equation was used to calculate concentration of dispersant in aqueous phase samples. The limit of detection for dispersant using this GPC method is approximately 0.05% by weight. Concentrations of potassium, sodium and

Table 1
Chemical properties of cement

Chemical analysis	Percentage by mass
SiO ₂	20.76
Al ₂ O ₃	4.35
Fe ₂ O ₃	3.17
CaO	63.1
MgO	2.96
SO ₃	2.75
K ₂ O	0.6
Na ₂ O	0.15
Total alkalis as Na ₂ O	0.54
Loss on Ignition	1.53
<i>Calcium sulfate phases</i>	
Gypsum	1.13
Hemihydrate	1.41
<i>Compound composition (Bogue calculation)</i>	
C ₃ S	57
C ₂ S	16
C ₃ A	6
C ₄ AF	10

Table 2
Concrete mixture proportions and properties

Low mix speed						High mix speed					
Batch	Cement (kg/m ³)	Water (kg/m ³)	Fine aggregate (kg/m ³)	Coarse aggregate (kg/m ³)	w/c	Batch	Cement (kg/m ³)	Water (kg/m ³)	Fine aggregate (kg/m ³)	Coarse aggregate (kg/m ³)	w/c
Plain	354	195	764	1087	0.55	Plain	353	195	761	1083	0.55
PC-2	352	143	810	1152	0.41	PC-2	351	143	807	1149	0.41
PC-1	351	134	816	1160	0.38	PC-1	351	136	817	1162	0.39
Batch	Cumulative		Slump (mm)	Air content (%)		Batch	Cumulative		Slump (mm)	Air content (%)	
	Mix time (min)	Drum rev.					Mix time (min)	Drum rev.			
Plain	7	126	205	1.0		Plain	7	126	205	1.4	
	27	213	185	–			12	216	195	–	
	47	300	170	–			17	306	185	–	
	67	387	160	1.3			22	396	165	1.0	
PC-2	7	126	210	2.2		PC-2	7	126	210	2.4	
	27	213	185	–			12	216	195	–	
	47	300	135	–			17	306	145	–	
	67	387	80	2.7			22	396	110	2.6	
PC-1	8	144	195	2.6		PC-1	7	126	210	2.3	
	27	229	125	–			12	216	130	–	
	48	314	70	–			17	306	80	–	
	68	399	40	2.5			22	396	75	2.4	



Fig. 1. Pressure filtration assembly.

calcium ions in aqueous phase were measured using a Varian SpectraAA 220 atomic absorption instrument. The concentration of sulfate ion was measured using a Dionix Ion Chromatograph.

2.3. Methods

2.3.1. Concrete batching and mixing

All concrete mixtures were prepared using the same sequence of material addition, i.e., approximately 70% of the mixing water and all of the dispersant were added to the mixer followed by coarse aggregate, cement, and fine aggregate. The remaining mix water was then added within the first several minutes of mixing to obtain the target slump. An initial mix time of 7 min (126 drum revolutions) was used to ensure complete incorporation of the dispersant. Mix PC-1-LS (LS—low speed mixing procedure) required 1 additional min of initial mixing along with a small amount of water to obtain the target starting slump. Following the initial mixing period, the air content, slump and concrete unit weight were determined and a sample was obtained for analytical testing. The material that was used to determine the concrete properties was then returned to the mixer. Two concrete batches were prepared for plain and both dispersant-treated concrete mixtures (6 mixtures total) and were subjected to one of two extended mixing procedures. The first batch was mixed at a drum rotation rate of 4 rpm and concrete was sampled for slump, air content and analytical testing at cumulative mixing times of 27, 47, and 67 min. The mixer speed was adjusted to 18 rpm for 30 s just prior to obtaining each sample. The second concrete batch was continuously mixed at 18 rpm and was sampled for slump, air content and analytical testing at cumulative mixing times of 12, 17, and 22 min. By accurately setting the mixing speed and controlling the mixing time, the cumulative drum revolutions at each sampling period were essentially the same for both mixing procedures. Given the potential variability of the slump test, two measurements

were performed by different operators at each test interval to obtain a more accurate determination of slump and the average slump value was recorded.

2.3.2. Concrete sample processing for analytical testing

At each sampling point, concrete was immediately screened through a 1.2 mm (#16 mesh) screen to separate the mortar fraction from the coarse aggregates. A 100 to 140 ml portion of mortar was placed in the pressure filtration apparatus for recovery of aqueous phase. Additionally, a 15 ml portion of mortar was washed with pure ethanol over a 45 μm (#325 mesh) screen to separate the cement fraction from the sand. The cement fraction was rinsed with pure ethanol using a Buchner funnel and filter paper and air-dried. This method of processing would also recover any sub-45 μm fines from the aggregate together with the cement fraction. The contamination of cement with aggregate fines was unavoidable and any effect from the fines should be equally present in all samples. The cement samples were stored in sealed polyethylene bottles until testing for specific surface area, non-evaporable water content and analysis by X-ray powder diffraction.

2.3.3. Pressure filtration

The aqueous phase was isolated from the mortar fraction by purging then pressurizing the apparatus with nitrogen gas to 550 kPa (80 psi). Filtrate was collected in a nitrogen purged plastic bottle until at least 2.5 g of aqueous phase was collected. Filtrate collection times varied between 1 and 4.5 min, with longer collection times being required with highly fluid mortars. The very fine particles in the highly dispersed mortars blocked pores in the filter membrane, which reduced filtration efficiency. When the filtration was complete, the collection bottle headspace was purged with nitrogen, the bottle sealed and analysis was promptly started. Between samples, the pressure filtration unit was cleaned, thoroughly dried and reassembled with a new filter membrane, and the unit was purged with nitrogen.

2.3.4. Aqueous phase analysis

Each sample of aqueous phase recovered from the pressure filtration apparatus was immediately submitted for testing using four analytical procedures. A 15 μl sample of aqueous phase was injected into the HPLC to determine the concentration of polycarboxylate dispersant. Reported values for percent adsorbed dispersant are based on the difference in measured dispersant concentration between the filtrate sample and a baseline sample of the dispersant in water corresponding to the dosage of the dispersant in the starting concrete mix. Approximately 1 g of aqueous phase was analyzed for hydroxyl ion concentration. The sample was accurately weighed, diluted with deionized water and immediately titrated with 0.05 N standard HCL to a phenolphthalein end point. Three approximately 0.5-g portions of aqueous phase were analyzed individually for

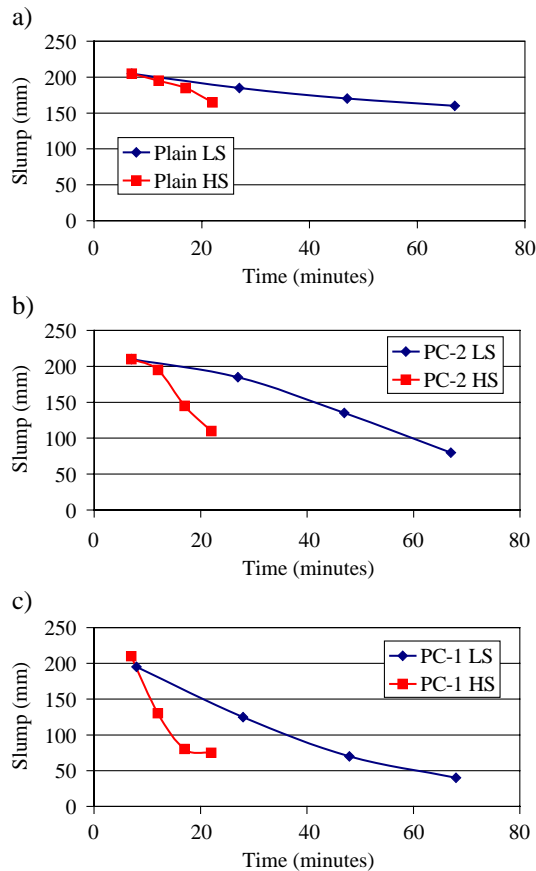


Fig. 2. Slump change over time for each treatment; (a) Plain, (b) PC-2, (c) PC-1 using low and high speed mixing procedures.

sodium, potassium, and calcium ion concentration using atomic absorption. Each sample was accurately weighed and immediately diluted and acidified with a 2% solution of nitric acid in deionized water. The diluted samples were immediately introduced to the AA instrument. Approximately 0.5 g of aqueous phase was analyzed for sulfate ion concentration using ion chromatography. The sample was accurately weighed, immediately diluted with deionized water and analyzed.

2.3.5. Solid phase analysis

Approximately 2 g of collected cement solids was used for specific surface area accessible by nitrogen using a multi-point BET technique. Samples were outgassed at 0.02 Torr and 20 °C until constant weight was achieved. Approximately 1 g of the collected cement solids was used for non-evaporable water content determination. The solids were placed in a conditioned crucible and brought to constant mass at 105 °C overnight. The crucibles were then fired at 1000 °C for 2 h. After cooling in a dessicator, the mass of material in the crucibles was determined. The non-evaporable water content was determined by difference, and degree of hydration was calculated. A few grams of the collected solids were analyzed by X-ray diffraction using a random powder pack to examine changes in

mineralogy that may have occurred during the early hydration.

3. Results and discussion

3.1. Concrete results

For any pair of slump determinations, individual values generally agreed within 20 mm of one another and all of the mixtures had initial starting slumps ranging from 195 to 210 mm (Table 2). Plain mixtures lost approximately 20% of their initial slump at the completion of testing, regardless of the mixing procedure as shown in Fig. 2a. PC-2 mixtures showed a more gradual rate of slump loss than PC-1 mixtures, ultimately losing 50–60% of their initial slump by the completion of the test (Fig. 2b). In contrast, PC-1 mixtures lost approximately 35% of their initial slump after the first extended mixing interval and had an ultimate loss of approximately 65–75% (Fig. 2c). Plotting the slump response against cumulative drum revolutions for each treatment (Fig. 3) reveals a remarkably similar result between the low and high speed mixing procedures, indicating that the change in slump was more a result of applied shear energy than elapsed time. The air contents for all of the mixtures ranged between 1.0 and 2.7% and were

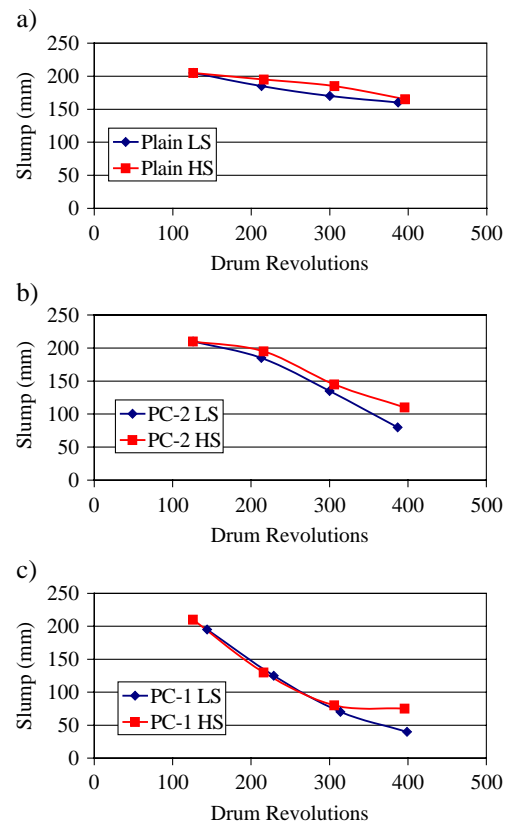


Fig. 3. Slump change versus cumulative drum revolutions for each treatment; (a) Plain, (b) PC-2, (c) PC-1.

Table 3
Dispersant depletion by time and mixer revolutions

Batch	Low mix speed			High mix speed		
	Cumulative		%PC adsorbed	Cumulative		%PC adsorbed
	Mix time (min)	Drum rev.		Mix time (min)	Drum rev.	
Plain	7	126	–	7	126	–
	27	213	–	12	216	–
	47	300	–	17	306	–
	67	387	–	22	396	–
PC-2	7	126	72	7	126	70
	27	213	78	12	216	76
	47	300	81	17	306	79
	67	387	83	22	396	80
PC-1	8	144	100	7	126	100
	27	229	100	12	216	100
	48	314	100	17	306	100
	68	399	100	22	396	100

fairly constant, differing by less than 0.5% for the duration of the extended mixing.

3.2. Aqueous phase depletion of PC

Analysis of filtrate solutions indicated both dispersants were rapidly adsorbed from the aqueous phase during the first several minutes of mixing. PC-1 dispersant showed higher binding characteristics than PC-2 dispersant, since PC-1 was not detected in any aqueous phase filtrates, whereas PC-2 was detected in every filtrate solution. The PC depletion results for both dispersants and for each mix condition are summarized in Table 3. Both mixing procedures involved an initial period of high speed mixing prior to the extended mixing periods at low or high speed mixing. This approach allowed duplicate determinations of initial dispersant depletion to be made. The replicate results were in good agreement for both dispersants, with only a small difference observed with PC-2. Aqueous phase depletion of PC-2 was characterized over time for both mixing procedures. Dispersant depletion rate was highest during the first few minutes of mixing and decreased with time for both mixing conditions. During the first extended mixing interval, an additional 6% depletion of PC-2 from aqueous phase was observed for both mixing procedures. An additional 3% depletion was observed during the second extended mixing interval and 1–2% further depletion was observed during the final extended mixing interval for both mixing procedures. It should be noted that the number of minutes comprising an extended mixing interval was different between the two mixing procedures, but the number of drum revolutions comprising an extended mixing interval was constant. The rate of PC-2 depletion was similar for both mixing procedures when based on mixing revolutions rather than time as shown in Fig. 4. Mixing speed (shear energy) influenced rate of dispersant depletion more than elapsed time in this study. The low speed mixing curve generally parallels the high speed mixing curve when PC adsorption percentage results are plotted against drum

revolutions. The influence of time on dispersant depletion was a small factor, since a divergence between the two curves would be expected if time were a significant factor during the time period under study. The low speed mixing procedure required 67 min to accumulate almost 400 drum revolutions and the high speed mixing procedure required only 22 min. The last sample tested from the low speed mixing procedure was about 45 min older than the last sample from the high speed mixing procedure, but PC-2 dispersant depletion values were very similar in both cases.

Dispersant depletion amounts were considerably higher in this concrete study when compared to typical results that have been generated in cement paste systems. To directly compare depletion amounts between paste and concrete, each polymer was tested in a paste system containing an identical dispersant dose, the same water to cement ratio and the same 7-min initial mix time that was used in the concrete study. The paste was mixed using a mechanical mixer at a stirring speed of approximately 700 rpm. PC-2 depletion in the paste system was about half of that observed in concrete, and PC-1 depletion was only 80 to 85% in the paste system versus 100% in the concrete study. Paste testing provides useful information as to the relative binding affinity of different PCs, but it can underestimate

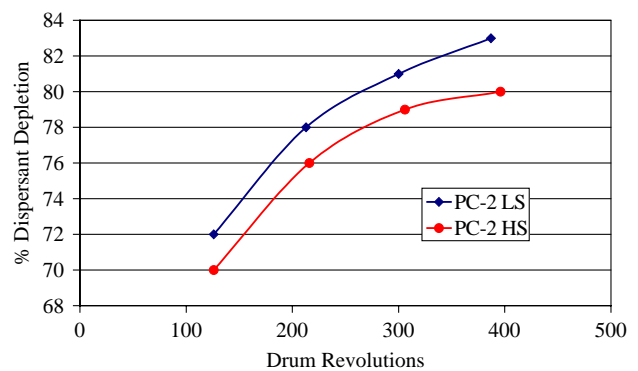


Fig. 4. PC-2 depletion versus drum revolutions for low and high mixing speeds.

the extent of dispersant depletion in concrete systems. Possible differences between adsorption amounts between concrete and paste systems may be caused by adsorption of dispersant on aggregate surfaces, dispersant adsorption onto fine particles from the aggregates, greater deflocculation of cement particles due to the grinding action of the aggregates or due to abrasion of hydration products from cement grains surfaces by moving aggregates to expose new binding surfaces.

3.3. Solution chemistry

The concentrations of ionic species that were measured in the aqueous phase are shown in Table 4. In general, higher initial concentrations of sulfate, hydroxyl, sodium, and potassium ions exist in the presence of the dispersants. Some of this difference can be attributed to the lower water content required to obtain the initial concrete slump, while the rest is likely due to the presence of the dispersants. Some sodium ion was introduced by the dispersants. The sodium content differences between the PCs were small and the sodium contribution by PC compared to the reported values, although measurable, were small. In the aqueous phase obtained from plain concrete that was mixed at low speed, a rise in hydroxyl ion concentration and a drop in sulfate ion concentration with mixing time offset a rise in potassium and calcium ion concentrations. These changes were less pronounced in the aqueous phase obtained from the companion plain concrete that was mixed at high speed, suggesting that changes in the aqueous phase chemistry of non water-reduced concrete are affected more strongly by time rather than drum revolutions. In the aqueous phase obtained from concrete that contained either PC-2 or PC-1 and was mixed at low speed, there were only small changes in ionic concentrations over time. These small changes in aqueous phase composition were also observed in the concrete that contained either PC-2 or PC-1 and was mixed at high speed. Thus the changes in slump retention and attributed differences in depletion of PC-2 or PC-1 are not related to compositional differences in the aqueous phase. From the experimental data, it cannot be determined to what extent the influence of mixing speed on the rate of slump loss was due to a mechanical effect or to an acceleration of chemical (hydration) reaction rate. It is possible that faster mixing speed caused an acceleration of chemical (hydration) reactions and the acceleration was due to a mechanical effect such as abrasion of hydration products from cement grain surfaces. This exploration of this topic was beyond the scope of this paper.

3.4. Cement paste results

The BET (N_2) surface area results are shown in Table 5. The results appear to be inconclusive. The surface area value decreased with extended mixing for the plain concrete mixed at high speed. The data for degree of

Table 4
Aqueous phase composition

Batch	Low mix speed						High mix speed							
	Cumulative			[SO ₄ ⁻²] (mmol/L)	[OH ⁻] (mmol/L)	[Na ⁺] (mmol/L)	[K ⁺] (mmol/L)	[Ca ⁺²] (mmol/L)	Cumulative					
	Mix time (min)	Drum rev.	Mix time (min)						Drum rev.					
Plain	7	126	50.34	71.00	28.36	112.86	22.77	7	126	49.98	77.50	28.37	111.72	23.07
	27	213	—	—	—	—	—	12	216	—	—	—	—	—
	47	300	—	—	—	—	—	17	306	—	—	—	—	—
	67	387	43.71	97.00	29.50	121.46	26.11	22	396	46.89	83.50	27.89	116.88	22.23
	7	126	68.82	87.70	42.55	161.03	21.47	7	126	69.20	83.00	43.00	161.74	23.93
PC-2	27	213	—	—	—	—	—	12	216	—	—	—	—	—
	47	300	—	—	—	—	—	17	306	—	—	—	—	—
	67	387	60.72	86.70	43.03	153.85	23.90	22	396	63.44	91.30	39.71	146.18	21.73
	8	144	69.30	87.70	42.48	148.59	20.22	7	126	73.40	88.50	43.62	155.73	21.14
	28	229	—	—	—	—	—	12	216	—	—	—	—	—
PC-1	48	314	—	—	—	—	—	17	306	—	—	—	—	—
	68	399	65.46	91.40	42.32	146.22	21.45	22	396	67.94	87.40	42.81	150.78	20.66

Table 5

Surface area and degree of hydration data

Mix	Low mix speed				High mix speed			
	Cumulative		Degree of Hydration (%)	BET (N ₂) SSA (m ² /g)	Cumulative		Degree of Hydration (%)	BET (N ₂) SSA (m ² /g)
	Mix time (min)	Drum rev.			Mix time (min)	Drum rev.		
Plain	7	126	9.2	8.1	7	126	9.8	7.5
	27	213	–	–	12	216	–	–
	47	300	–	–	17	306	–	–
	67	387	11.1	8.3	22	396	11.2	5.3
PC-2	7	126	8.5	4.2	7	126	7.7	6.4
	27	213	–	–	12	216	–	–
	47	300	–	–	17	306	–	–
	67	387	12.3	5.5	22	396	12.9	9.1

hydration of the cement, α , are also shown in Table 5. The values are may have been slightly elevated by the presence in the cement paste of dolomite powder from the coarse aggregate. In all cases, α increased with mixing time from the initial measurement to the final measurement. The degree of hydration values were similar for PC-1 and PC-2 mixtures and showed similar increases over time with both mixing procedures. The amount of hydration that occurred during the study period was small and it was affected in a similar manner by the two dispersants. The amount of hydration that occurred during the study was not a significant factor behind the different slump retention results for the two dispersants. For the concrete that contained either PC-2 or PC-1, slightly more hydration had occurred by the end of the mixing period, compared to the concrete that did not contain dispersant, regardless of the mixing procedure. Plots from the X-ray diffraction testing were generated for the initial and final cement paste samples from each set. A comparison of the initial and final X-ray diffraction pattern revealed little differences, except for a diminishment of the main peak attributed to gypsum over this time period.

4. Conclusions

1. Dispersant structure and the amount of applied shear energy influenced the rate of dispersant depletion from the aqueous phase and the rate of dispersant depletion influenced concrete workability retention.
2. Slump retention was influenced by the amount of dispersant remaining in the aqueous phase. Higher rates of slump loss were observed with a dispersant that was rapidly adsorbed from the aqueous phase and better slump retention was observed with a dispersant that was adsorbed more slowly from the aqueous phase.
3. The higher charge density dispersant (PC-1) was depleted faster than the lower charge density dispersant

(PC-2). PC-1 was completely adsorbed from the aqueous phase and approximately 70% of PC-2 was adsorbed from the aqueous phase at the first analysis point. During extended mixing, the rate of PC-2 depletion was more strongly influenced by the number of completed drum revolutions than elapsed time.

4. Dispersant depletion levels were much higher in a concrete system compared to a cement paste system. Relative differences in dispersant binding characteristics can be determined in paste systems and those differences in paste correlated with concrete findings, but paste systems underestimate the extent of dispersant depletion in concrete systems. The differences between dispersant adsorption amounts between paste and concrete systems may be due to differences in available surface area for dispersant binding.
5. The addition of PC dispersants appears to diminish changes that occur over time in the solution chemistry of the concrete aqueous phase, when compared to changes that occur over time in the composition of the plain concrete aqueous phase. In the presence of PC-2 or PC-1, the aqueous phase ionic composition was not notably different at any particular measurement point. This suggests that depletion of dispersant and associated slump response was not attributed to changes in the ionic composition of the aqueous phase.
6. Regarding cement hydration, measurable changes in surface area of hydrated cement, degree of hydration, and phase composition as determined by X-ray diffraction were difficult to detect over the small time frame of this study, independent of the presence of a dispersant.

Acknowledgements

The authors would like to thank Frank Danko, Meiling Gong, Frank Ong and Samy Shendy for their help in

conducting the numerous analytical and concrete tests that were necessary to support this study.

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