Stability and Quality of Air Void Systems in Concretes with Superplasticizers

By

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STABILITY AND QUALITY OF AIR VOID SYSTEMS IN CONCRETES WITH SUPERPLASTICIZERS

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1.1 Overview

Superplasticizers are an excellent tool in reducing the amount of cement in modern concrete. Polycarboxylate-based (PC) superplasticizers are a relatively new tool in admixture technology. These comb-shaped molecules have allowed researchers to repel cement grains so effectively as to allow them to produce self-consolidating concrete (SCC). These admixtures have a linear water reduction response with increased dosage and do not delay the set and strength gain of the concrete mixtures with recommended dosage rates.

Due to the relative youth of these admixtures, little research has been completed concerning their long-term impact on concrete freeze-thaw durability. One of the challenges of evaluating freeze-thaw durability is time. Actual field damage may take decades to observe. Therefore lab testing must be accelerated in order to predict performance. The ASTM Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing (C666) allows a test specimen to undergo a cycle of freeze-thaw in approximately four hours. While this rapidity is convenient, research suggests these cycles may be harsher than most found in nature.

This research, funded by the Oklahoma Transportation Center, evaluated concretes with 5 different PCs for freeze-thaw durability. The results surprisingly indicated that some concretes containing both PC and enough fresh air to expect satisfactory performance indeed failed C666.

This research therefore also evaluated the stability of the air-void system, as well as other parameters, over time.

Chapter 2: Stability and Quality of Air Void Systems in Concretes with Superplasticizers

2.1 Introduction

When air-entrained concrete is made, bubbles are purposely created in the fresh concrete. The bubbles leave important voids in the hardened concrete that are crucial to frost durability. The presence of these voids will affect the workability, consistency, bleeding, and yield of the fresh material, as well as the density, strength, and most significantly, the frost durability of the hardened concrete. The effects these voids have on frost durability are dependent not only on their total volume, but also on their size distribution and dispersion throughout the paste of the hardened concrete.

The void system is created by adding an air-entraining agent during mixing of the fresh concrete. Careful production and placement methods must be used to preserve these voids in the hardened concrete. Air-entraining agents (AEAs) reduce the surface tension of water, allowing more and smaller bubbles to form and stabilize during mixing. While the concrete is still plastic the void system is dynamic, and voids are able to travel, segregate, coalesce, change size, and escape the mixture entirely.

The characteristics of air-void systems in hardened concrete can be evaluated with ASTM C457, *Microscopical Determination of Parameters of the Air-Void System in Hardened*

Concrete. The methods include calculations for two key parameters in determining the quality of an air-void system, spacing factor and specific surface area. These parameters were first determined by T. C. Powers (1954a, 1954b). ACI 201 *Guide to Durable Concrete* recommends a maximum spacing factor of 0.008 in. and a specific surface area greater than 600 $in.^{-1}$ for frost durability (2008). The Canadian Standards Association (2009) has suggested that a spacing factor can be as high as 0.010 in. from a lot of concrete as long as the average for the element is not higher than 0.009 in. It is common to specify a total volume of air in the concrete based on work by Klieger (1952, 1956). Unfortunately the mixtures investigated by Klieger are very different from modern mixtures. Despite this the *Building Code Requirements for Structural Concrete* recommends that 6% air content is needed for frost durability for concrete with ¾" maximum nominal aggregate (ACI 2011). Various methods are used to test this air content, including the *Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method* (ASTM C231), the *Standard Test Method for Air Content of Freshly Mixed Concrete by the Volumetric Method* (ASTM C173), and the *Standard Test Method for Density (Unit Weight), Yield, and Air Content (Gravimetric) of Concrete* (ASTM C138). One challenge with all of these techniques is that they are only able to measure the volume and not the void distribution.

Polycarboxylate (PC) superplasticizers were first reported for hydraulic cement in 1998 (Moreau, Lu, Bury, 1998). PCs are comb-shaped molecules that cause cement grains to repel each other through steric hindrance (Ramachandran 1995). These admixtures act as a water reducer and have been widely used in special applications, such as self-consolidating concrete (SCC), as they have the ability to reduce the water demand of the mixture by at least 30%

without impacting the set time and with a linear dosage response (Jeknavorian 2011; Ramachandran 1996). Recently, PCs have started to be proposed for use in smaller dosages to replace midrange water reducers.

Unchecked, these admixtures stabilize a significant amount of air during mixing that would greatly reduce the strength of the mixture (Zhang 2005). To combat this, a defoaming chemical is added to reduce these bubbles (Kuo 2012). These admixtures allow concrete mixtures to be prepared with less cement, leading to improvements in cost, sustainability, and durability. These admixtures are powerful tools that have become an important part of the concrete industry.

There have been a few reports from the field about air-void systems reducing in volume over time and challenges obtaining the recommended spacing factors (Lankard, 2006). This is problematic because quality control for new concrete is typically governed by fresh measurements instead of by hardened air-void analysis. If air-void systems are being altered by these materials or if significant volumes are being lost over time then recommendations made by Klieger and ACI 318 may be invalid. Another consideration is the effect these chemicals will have on the air-void system during transport. Currently very little systematic laboratory data exists on this topic. The goal of this study is to examine and compare the stability, air-void quality, and freeze-thaw performance of concrete both with and without PCs.

2.2 Experimental Methods

2.2.1 Materials

All of the concrete mixtures described in this paper were prepared using a Type I/II cement that meets the requirements of ASTM C150. The oxide analysis is shown below in Table 1 and is found from X-ray fluorescence (XRF) analysis. The phases were calculated with the Bogue equations (ASTM C150). The aggregates used were locally available dolomitic limestone and sand used in commercial concrete and proven to be frost durable. The rock was a ¾” maximum nominal size aggregate, and both the rock and sand met the requirements of ASTM C33. Admixtures used in this study, including AEAs and PCs, met the requirements of ASTM C260, C494, and/or C1017. Admixtures used in this study are described in Table 2.

Table 1. Oxide analysis for cement used in this study.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	C_3S	C_3A	C_2S	C_4AF
20.1%	4.8%	2.9%	63.0%	2.0%	0.3%	0.3%	3.0%	58.0%	7.9%	14.1%	9.1%

Table 2. Admixtures used in this study.

Abbreviation	Chemical Family Name	ASTM	Application
PC1	Carboxylated Polyether	C494F; C1017 I	Superplasticizer
PC2	Carboxylated Polyether	C494 A, F; C1017 I	Superplasticizer
PC3	Carboxylated Polymer	C494 A, F; C1017 I	Superplasticizer
PC4	Polyacrylate Solution	C494 A, F	Superplasticizer
PC5	Polyacrylate Solution	C494 A, F; C1017 I	Superplasticizer
WROS	Wood Rosin	C260	Air-Entrainer
SYNTH	Synthetic Chemical Combination	C260	Air-Entrainer
VR	Vinsol Resin	C260	Air-Entrainer

2.2.2 Procedure

All of the materials for mixing were stored at 73° F for at least 24 hours to bring them to a constant temperature before being combined in the mixer. Both the coarse and fine aggregate for each mixture were sampled from an open storage facility and had variable moisture contents. The moisture content of each sample was determined and corrected prior to batching the mixtures. The coarse and fine aggregates were blended separately to bring them to a uniform moisture content. The blended aggregates were sampled, and these samples were dried in an oven to determine the amount of water they contained. This information was used to modify the batching weights from the base mixture design to ensure that the expected amount of water was actually present in the mixture.

The method of preparing the mixtures is herein described. All of the aggregate, both coarse and fine, are charged into the mixer along with approximately two-thirds of the mixing water. This combination is mixed for three minutes. Next any clumped fine aggregate is removed from the walls of the mixer. Then the cement is loaded into the mixer, followed by the remaining mixing water. The mixer is turned on for an additional three minutes. Once this mixing period is complete, the mixture is left to "rest" for the following two minutes while the buildup of material along the walls is removed. Next the mixer is started and the admixtures are added. If any superplasticizer is to be used in the mixture, it is added first and allowed thirty seconds of mixing before the air-entraining agent is added. Once all the admixtures are in the mixer, it is allowed to run for the remainder of the three minutes.

The mixture designs are listed in Table 3 in pounds per cubic yard. The mixtures are referred to by their water-cement ratio thereafter.

Table 3. Mixing proportions in pounds on a cubic yard basis.

CA	FA	Water	Cement	w/cm
1850	1203	275	611	0.45
1815	1180	301.6	599.5	0.50
1907	1240	231	630	0.37

2.2.3 Sampling and Testing

A standard procedure was used to sample and test the stability and frost durability of the concrete. Mixtures not subjected to the same procedure are noted in the data section. The procedure has been summarized in Table 4.

All times reported in this study were taken after the eight minute mixing period. All times in Table 4 are measured after mixing is complete. Immediately after mixing (referred to as 0 minutes) the mixture is tested for slump (ASTM C143), unit weight (ASTM C138), and fresh air content (ASTM C231). A modified C231 specimen is prepared simultaneously with the C138 and C231 sample in order to ensure they have the same time dependent properties. Next, samples are prepared for freeze-thaw durability testing (ASTM C666) and hardened air-void analysis (ASTM C457). ASTM C666 does not clearly define freeze thaw failure, however some guidance is given in admixture standards ASTM C260, ASTM C494, and ASTM C1017. These standards recommend that the ASTM C666 durability factor of a mixture with and without an admixture should not differ by more than 20%. If this criterion is used to evaluate the performance of a mixture in the ASTM C666 test then the limiting durability factor would be between 70% and 80% (Ley 2007). For this study, failure of ASTM C666 will be defined as having a durability factor (DF) less than 80%.

2.2.3.1 Modified Pressure Meter

A novel testing method used in this work is a modified version of the ASTM C231 concrete pressure meter test. This test is designed to measure the change in air content over time in a consolidated sample of concrete. While preparing the sample for measuring the fresh air content by ASTM C231, the researcher simultaneously prepares an additional quarter cubic foot unit weight bucket following the same method. One lift is placed for the standard method, and then one lift is prepared for the modified method. This helps ensure the time dependent properties of each sample are as close to each other as possible. The difference between the two samples is that the unit weight container for the modified test method is lined with a thin plastic membrane, and the sample is not measured immediately, but is allowed to sit undisturbed for two hours. The membrane is added to keep the aluminum bucket from reacting chemically with the fresh concrete. The membrane was shown to not impact the readings of the pressure meter by checking the calibration of the meter with and without the membrane. The sample was allowed to sit for 120 minutes to obtain as much information as possible about the change of the air-void system before initial set occurs.

Table 4. Tests and Samples Collected over 120 Minutes.

ASTM	Description	Time After Mixing				
		0 min	30 min	60 min	90 min	120 min
C143	Slump	X	X	X	X	X
C138	Unit Weight	X	X	X	X	X
C231	Pressure Meter	X		X		X
N/A	Modified Pressure Meter	*				X
C666	Freeze Thaw	X		X		
C457	Hardened Air-void Analysis	X		X		

*Modified pressure meter samples are prepared at 0 minutes and evaluated at 120 minutes.

Slump and unit weight were both measured every 30 minutes to monitor their changes over time. All samples were consolidated by rodding as per the ASTM procedure. Air content was sampled every 60 minutes. This coincides with the preparation of the freeze-thaw beams at 0 and 60 minutes and provides a comparison for the modified C231 test. One mixture was tested without being sampled at all between 0 and 120 minutes. This was done to investigate the impact of sampling the concrete on the slump and air content over time. This also allowed the 120 minute samples to be collected from a larger volume of material, rather than the small amount remaining during the typical test.

2.2.3.2 Hardened Air-void Analysis Sample Preparation

The hardened air samples were cut into ¾” thick slices using a concrete saw. A mixture of lacquer and acetone was applied to harden the surface to protect the air-voids from damage during polishing. A set of diamond grit concrete polishing discs were used to prepare the samples’ surfaces, as per ASTM C457.

After the polishing was complete, each sample was inspected under a stereomicroscope to ensure aggregates and paste had been lapped to the same elevation and there was a high quality finish on the specimen. After the specimen had received an acceptable polish, then they were soaked in acetone to remove the remaining lacquer. The prepared sample surface was then colored solid with a black permanent marker then dried for 3 hours. A second coat of black marker was then applied in the perpendicular direction to the first coat and the sample dried for 8 hours. A thin layer of barium sulfate was pressed on the colored surface twice with a rubber stopper to force the white powder into the voids. This technique is described in EN 480-11. This left the surface of the concrete black and the voids white. Since the analysis is concerned only with the voids in the paste, the voids in the aggregate must be masked and were therefore colored with a fine permanent ink pen under a stereomicroscope. A final inspection was made of the surface to ensure that voids in the paste are white and all other areas in the sample are black. A sufficiently polished sample and a finished sample can be seen in Figures 1 and 2. This technique is outlined in detail in Ley (2007) and has been used by several other researchers (Jakobsen et al 2006, Sutter 2002, Carlson 2005, Peterson et al 2007).

Once the voids in the paste have been preferentially marked, it is possible to use this contrast to determine the air-void parameters of the mixture. The research team used the Rapid Air 457 from Concrete Experts, Inc. This machine completes an automated linear traverse analysis on the sample by using a CCD camera to image the surface and an automated stage for precise movement. Image analysis is then used to discern voids (white) from other portions of the sample (dark). A single threshold value of 145 was used for all of the samples that has been shown to be satisfactory with the sample preparation materials and processes used (Ley 2007). This technique requires that the volume of paste be given. This was determined from the batch weights for each concrete mixture design. For the results of the hardened air-void analysis reported in this paper, chords smaller than 30 μm were not included in as they are not easily detected by a human during an ASTM C 457 analysis. By excluding these chords, the air-void parameters determined by the hardened air-void analysis are better comparable to previously reported values of ASTM C 457 results. This has been done previously by many researchers (Jakobsen et al 2006, Ley 2007, Peterson et al 2009, Ramezanianpour & Hooton 2010).

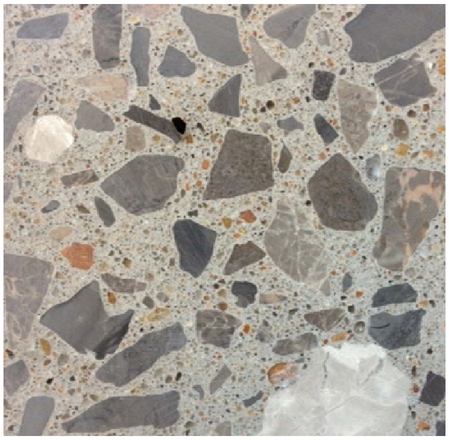

Figure 1. Satisfactorily lapped sample.

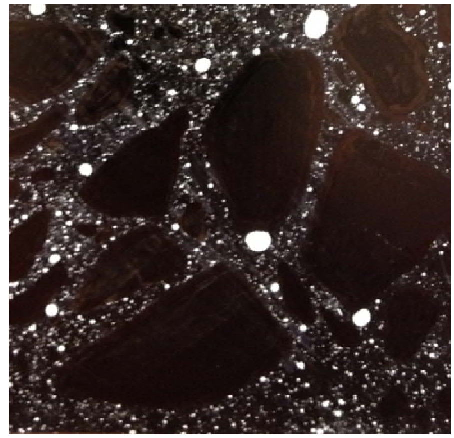

Figure 2. Finished sample.

2.2.4 Mixture Selection

Mixtures investigated were placed into four groups. Mixtures in Group 1 include a direct comparison between mixtures with a 0.45 w/cm with a wood rosin AEA and a mixture with a wood rosin AEA and a PC. These mixtures were designed so that they had a slump of about 3” without a PC and a slump of 10” once the PC was added. The AEA was added in all of these mixtures to obtain a target air content of 5 ± 1%. These targets were chosen as they are common values for acceptable air content for field concrete. The third mixture in Group 1 is identical to the mixture with the wood rosin and PC, but it was only sampled at 0 and 120 minutes. This mixture was included to investigate the impact of sampling the bulk material over time. It also allowed the 120 minute samples to be taken from a larger volume of material rather than what typically remained at the end of testing.

Group 2 contained three mixtures that all used the same PC and either a wood rosin, Vinsol resin, or a synthetic AEA. This allowed the performance of different AEAs to be compared with a constant PC.

The five mixtures investigated in Group 3 all contained a wood rosin AEA but different PCs. A wood rosin was chosen as it is the most commonly used AEA in practice. This group of mixtures compared five different PCs with a constant AEA.

Group 4 has five mixtures which were selected to have different levels of workability. These mixtures were investigated to determine if the stability of the air-void system was a function of the viscosity or workability of the mixture. This included a mixture with a 0.50 w/cm and wood rosin AEA and no PC and one with a 0.37 w/cm and a PC. The mixture with the 0.37 w/cm lost workability too rapidly to be tested after 60 minutes. The test procedure was therefore modified to only last 60 minutes. A mixture was also included with a half dosage of PC.

2.3 Results

The data collected from this study is summarized in Tables 5 through 8. The Rapid Freeze/Thaw data is either reported as the average and range of the durability factor between two samples, or the average number of cycles the samples underwent before it was unable to register a dynamic modulus. The column Normalized Change is the difference between the first measurement at 0 minutes and the last measurement, usually at 120 minutes, divided by the measurement a 0 minutes, reported as a percentage. In the case of the hardened air data as well as all values for the 0.37 w/cm mixture, the Normalized Change is calculated using the 60 minute measurement in place of the 120 minute measurement.

Table 5 shows data collected for Group 1 mixtures, Table 6 shows data collected for Group 2 mixtures, Table 7 shows data collected for Group 3 mixtures, and Table 8 shows data collected for Group 4 mixtures.

Table 5. Summary of data collected from Group 1 testing.

Mixture ID	w/cm	PC Dosage (oz/cwt)	AEA Dosage (oz/cwt)	Test		Time After Mixing Completed 0 min. (A)	30 min.	60 min.	90 min.	120 min. (B)	Normalized Change ((B-A)/A)x100
WROS Only	0.45	0	0.66	Slump, in. (C143)		2.75	1.75	1.25	1.25	0.75	-72.7%
				Air Content	Gravimetric (C138)	2.9%	2.5%	2.2%	1.9%	1.0%	-64.9%
					Pressure Meter (C231)	3.5%	-	3.5%	-	2.4%	-31.4%
					Modified C231	-	-	-	-	3.3%	-5.7%
				Rapid Freeze/Thaw (C666)*		97 ± 3%	-	97 ± 3%	-	-	-
				Hardened Air (C457)	Hardened Air Content	2.7%	-	3.6%	-	-	32.2%†
					Spacing Factor, in.	0.0086	-	0.0094	-	-	9.3%†
					Specific Surface, in.$^{-1}$	748	-	601	-	-	-19.8%†
PC1 + WROS	0.45	4.96	0.32	Slump, in. (C143)		8.75	3.5	2.5	1.5	1.5	-82.9%
				Air Content	Gravimetric (C138)	4.2%	1.6%	1.7%	1.0%	1.3%	-69.6%
					Pressure Meter (C231)	4.5%	-	2.4%	-	2.4%	-46.7%
					Modified C231	-	-	-	-	4.1%	-8.9%
				Rapid Freeze/Thaw (C666)*		(137)	-	(66)	-	-	-
				Hardened Air (C457)	Hardened Air Content	5.3%	-	2.5%	-	-	-51.8%†
					Spacing Factor, in.	0.0130	-	0.0135	-	-	3.8%†
					Specific Surface, in.$^{-1}$	366	-	572	-	-	56.6%†
PC1 + WROS Undist.	0.45	4.96	0.33	Slump, in. (C143)		10	-	-	-	1.5	-85.0%
				Air Content	Gravimetric (C138)	5.1%	-	-	-	1.6%	-68.4%
					Pressure Meter (C231)	6.0%	-	-	-	2.5%	-58.3%
					Modified C231	-	-	-	-	5.3%	-11.7%
				Rapid Freeze/Thaw (C666)*		-	-	-	-	-	-
				Hardened Air (C457)	Hardened Air Content	7.6%	-	-	-	-	-
					Spacing Factor, in.	0.0099	-	-	-	-	-
					Specific Surface, in.$^{-1}$	371	-	-	-	-	-

*ASTM C666 results are listed as the average DF and range (%) or as the average number of cycles completed before testing could not continue.
†Normalized Change for this value is measured from 0 to 60 minutes.

Table 6. Summary of data collected from Group 2 testing.

Mixture ID	w/cm	PC Dosage (oz/cwt)	AEA Dosage (oz/cwt)	Test		Time After Mixing Completed 0 min. (A)	30 min.	60 min.	90 min.	120 min. (B)	Normalized Change ((B-A)/A)x100
PC1 + WROS	0.45	4.96	0.32	Slump, in. (C143)		8.75	3.5	2.5	1.5	1.5	-82.9%
				Air Content	Gravimetric (C138)	4.2%	1.6%	1.7%	1.0%	1.3%	-69.6%
					Pressure Meter (C231)	4.5%	-	2.4%	-	2.4%	-46.7%
					Modified C231	-	-	-	-	4.1%	-8.9%
				Rapid Freeze/Thaw (C666)*		(137)	-	(66)	-	-	-
				Hardened Air (C457)	Hardened Air Content	5.3%	-	2.5%	-	-	-51.8%†
					Spacing Factor, in.	0.0130	-	0.0135	-	-	3.8%†
					Specific Surface, in.$^{-1}$	362	-	572	-	-	58.2%†
PC1 + VR	0.45	4.96	0.31	Slump, in. (C143)		9.75	5.5	4	2.25	1.5	-84.6%
				Air Content	Gravimetric (C138)	4.8%	2.1%	1.0%	1.2%	1.1%	-77.6%
					Pressure Meter (C231)	5.5%	-	2.5%	-	3.0%	-45.5%
					Modified C231	-	-	-	-	4.3%	-21.8%
				Rapid Freeze/Thaw (C666)*		(190)	-	(113)	-	-	-
				Hardened Air (C457)	Hardened Air Content	3.8%		2.4%		-	-35.6%†
					Spacing Factor, in.	0.0118		0.0230		-	94.9%†
					Specific Surface, in.$^{-1}$	468		292		-	-37.6%†
PC1 + SYNTH	0.45	4.96	0.09	Slump, in. (C143)		9.75	7	5	3.5	1.5	-84.6%
				Air Content	Gravimetric (C138)	4.8%	3.1%	2.0%	1.4%	1.1%	-76.5%
					Pressure Meter (C231)	5.8%	-	3.2%	-	2.9%	-50.0%
					Modified C231	-	-	-	-	5.4%	-6.9%
				Rapid Freeze/Thaw (C666)*		(173)	-	(123)	-	-	-
				Hardened Air (C457)	Hardened Air Content	4.2%	-	3.1%	-	-	-25.7%†
					Spacing Factor, in.	0.0109	-	0.0110	-	-	0.9%†
					Specific Surface, in.$^{-1}$	484	-	550	-	-	13.6%†

*ASTM C666 results are listed as the average DF and range (%) or as the average number of cycles completed before testing could not continue.
†Normalized Change for this value is measured from 0 to 60 minutes.

Table 7. Summary of data collected from Group 3 testing.

Mixture ID	w/cm	PC Dosage (oz/cwt)	AEA Dosage (oz/cwt)	Test		Time After Mixing Completed: 0 min. (A)	30 min.	60 min.	90 min.	120 min. (B)	Normalized Change ((B-A)/A)x100
PC1 + WROS	0.45	4.96	0.32	Slump, in. (C143)		8.75	3.5	2.5	1.5	1.5	-82.9%
				Air Content	Gravimetric (C138)	4.2%	1.6%	1.7%	1.0%	1.3%	-69.6%
					Pressure Meter (C231)	4.5%	-	2.4%	-	2.4%	-46.7%
					Modified C231	-	-	-	-	4.1%	-8.9%
				Rapid Freeze/Thaw (C666)*		(137)	-	(66)	-	-	-
				Hardened Air (C457)	Hardened Air Content	5.3%	-	2.5%	-	-	-51.8%†
					Spacing Factor, in.	0.0130	-	0.0135	-	-	3.8%†
					Specific Surface, in.$^{-1}$	362	-	572	-	-	58.2%†
PC2 + WROS	0.45	5.40	0.26	Slump, in. (C143)		9	6.5	5.2	3.5	1	-88.9%
				Air Content	Gravimetric (C138)	3.8%	1.9%	1.1%	0.5%	1.0%	-74.3%
					Pressure Meter (C231)	5.0%	-	2.3%	-	2.3%	-54.0%
					Modified C231	-	-	-	-	4.8%	-5.0%
				Rapid Freeze/Thaw (C666)*		(105)	-	(105)	-	-	-
				Hardened Air (C457)	Hardened Air Content	3.4%	-	2.0%	-	-	-39.6%†
					Spacing Factor, in.	0.0143	-	0.0180	-	-	25.9%†
					Specific Surface, in.$^{-1}$	407	-	404	-	-	-0.7%†
PC3 + WROS	0.45	6.45	0.15	Slump, in. (C143)		7.75	5.25	4	2.75	1.5	-80.6%
				Air Content	Gravimetric (C138)	5.2%	4.4%	3.9%	3.3%	2.7%	-47.7%
					Pressure Meter (C231)	5.7%	-	4.4%	-	3.3%	-42.1%
					Modified C231	-	-	-	-	5.6%	-1.75%
				Rapid Freeze/Thaw (C666)*		97 ± 3%	-	100 ± 0%	-	-	-
				Hardened Air (C457)	Hardened Air Content	5.8%	-	4.2%	-	-	-27.8%†
					Spacing Factor, in.	0.0068	-	0.0087	-	-	27.9%†
					Specific Surface, in.$^{-1}$	667	-	605	-	-	-9.3%†
PC4 + WROS	0.45	9.73	0.07	Slump, in. (C143)		7	4.25	3	2	1.5	-78.6%
				Air Content	Gravimetric (C138)	5.4%	4.0%	2.6%	2.6%	1.9%	-64.7%
					Pressure Meter (C231)	5.5%	-	3.1%	-	2.7%	-50.9%
					Modified C231	-	-	-	-	5.2%	-5.45%
				Rapid Freeze/Thaw (C666)*		96 ± 0%	-	92 ± 2%	-	-	-
				Hardened Air (C457)	Hardened Air Content	4.8%	-	2.7%	-	-	-43.7%
					Spacing Factor, in.	0.0084	-	0.0098	-	-	16.7%
					Specific Surface, in.$^{-1}$	595	-	658	-	-	10.6%
PC5 + WROS	0.45	4.87	0.61	Slump, in. (C143)		9.25	5.25	3.125	1.625	0.875	-90.5%
				Air Content	Gravimetric (C138)	5.0%	2.9%	1.8%	1.4%	1.3%	-74.3%
					Pressure Meter (C231)	5.2%	-	3.0%	-	2.5%	-51.9%
					Modified C231	-	-	-	-	4.0%	-23.08%
				Rapid Freeze/Thaw (C666)*		(300)	-	(240)	-	-	-
				Hardened Air (C457)	Hardened Air Content	3.8%	-	2.6%	-	-	-30.3%†
					Spacing Factor, in.	0.0099	-	0.0097	-	-	-2.0%†
					Specific Surface, in.$^{-1}$	559	-	581	-	-	3.9%†

*ASTM C666 results are listed as the average DF and range (%) or as the average number of cycles completed before testing could not continue.
†Normalized Change for this value is measured from 0 to 60 minutes.

Table 8. Summary of data collected from Group 4 testing.

Mixture ID	w/cm	PC Dosage (oz/cwt)	AEA Dosage (oz/cwt)	Test		Time After Mixing Completed 0 min. (A)	30 min.	60 min.	90 min.	120 min. (B)	Normalized Change ((B-A)/A)x100
WROS Only	0.45	0	0.66	Slump, in. (C143)		2.75	1.75	1.25	1.25	0.75	-72.7%
				Air Content	Gravimetric (C138)	2.9%	2.5%	2.2%	1.9%	1.0%	-64.9%
					Pressure Meter (C231)	3.5%	-	3.5%	-	2.4%	-31.4%
					Modified C231	-	-	-	-	3.3%	-5.7%
				Rapid Freeze/Thaw (C666)*		97 ± 3%	-	97 ± 3%	-	-	-
				Hardened Air (C457)	Hardened Air Content	2.7%	-	3.6%	-	-	32.2%†
					Spacing Factor, in.	0.0086	-	0.0094	-	-	9.3%†
					Specific Surface, in.$^{-1}$	748	-	601	-	-	-19.8%†
WROS Only + High Slump	0.50	0	0.69	Slump, in. (C143)		6.25	-	-	-	-	-
				Air Content	Gravimetric (C138)	4.6%	4.0%	3.5%	3.1%	2.2%	-52.0%
					Pressure Meter (C231)	5.5%	-	4.5%	-	3.8%	-30.9%
					Modified C231	-	-	-	-	5.3%	-4.5%
				Rapid Freeze/Thaw (C666)*		97 ± 3%	-	93 ± 0%	-	-	-
				Hardened Air (C457)	Hardened Air Content	5.2%	-	3.7%	-	-	-29.2%†
					Spacing Factor, in.	0.0063	-	0.0087	-	-	38.1%†
					Specific Surface, in.$^{-1}$	768	-	654	-	-	-14.8%†
PC1 + WROS	0.45	4.96	0.32	Slump, in. (C143)		8.75	3.5	2.5	1.5	1.5	-82.9%
				Air Content	Gravimetric (C138)	4.2%	1.6%	1.7%	1.0%	1.3%	-69.6%
					Pressure Meter (C231)	4.5%	-	2.4%	-	2.4%	-46.7%
					Modified C231	-	-	-	-	4.1%	-8.9%
				Rapid Freeze/Thaw (C666)*		(137)	-	(66)	-	-	-
				Hardened Air (C457)	Hardened Air Content	5.3%	-	2.5%	-	-	-51.8%†
					Spacing Factor, in.	0.0130	-	0.0135	-	-	3.8%†
					Specific Surface, in.$^{-1}$	366	-	488	-	-	33.4%†
Half PC1 + WROS	0.45	2.48	0.28	Slump, in. (C143)		6	2.75	2	2	-	-66.7%
				Air Content	Gravimetric (C138)	6.8%	2.9%	2.2%	2.1%	1.6%	-77.2%
					Pressure Meter (C231)	7.2%	-	3.25%	-	2.5%	-65.3%
					Modified C231	-	-	-	-	6.2%	-13.9%
				Rapid Freeze/Thaw (C666)*		69 ± 5%	-	(300)	-	-	-
				Hardened Air (C457)	Hardened Air Content	5.9%	-	4.0%	-	-	-32.7%†
					Spacing Factor, in.	0.0099	-	0.0105	-	-	6.1%†
					Specific Surface, in.$^{-1}$	453	-	514	-	-	13.4%†
PC1 + WROS (0.37) 1HR	0.37	4.96	3.91	Slump, in. (C143)		4.5	2	0.875	-	-	-80.6%†
				Air Content	Gravimetric (C138)	9.1%	7.2%	5.3%	-	-	-42.1%†
					Pressure Meter (C231)	8.5%	7.2%	5.5%	-	-	-35.3%†
					Modified C231	-	-	8.5%	-	-	0.0%†
				Rapid Freeze/Thaw (C666)*		97 ± 0%	-	86 ± 8%	-	-	-
				Hardened Air (C457)	Hardened Air Content	5.3%	-	3.3%	-	-	-37.2%†
					Spacing Factor, in.	0.0087	-	0.0106	-	-	21.8%†
					Specific Surface, in.$^{-1}$	523	-	533	-	-	2.0%†

*ASTM C666 results are listed as the average DF and range (%) or as the average number of cycles completed before testing could not continue.
†Normalized Change for this value is measured from 0 to 60 minutes.

Figure 3 shows the changes in slump over time for mixtures from Groups 1 and 3. These mixtures were chosen as they compare the general behavior of mixtures with and without PCs with a wood rosin AEA. The mixtures not shown had a similar performance and so are not shown for clarity. The y-axis shows slump normalized to the measurement at 0 minutes. Values plotted are percent of original slump versus the time of the measurement after mixing. The undisturbed mixture does not have the points at 0 and 120 minutes connected because values were not collected between these times. As can be seen, all of the mixtures showed significant slump loss over time. This was common for all of the mixtures investigated.

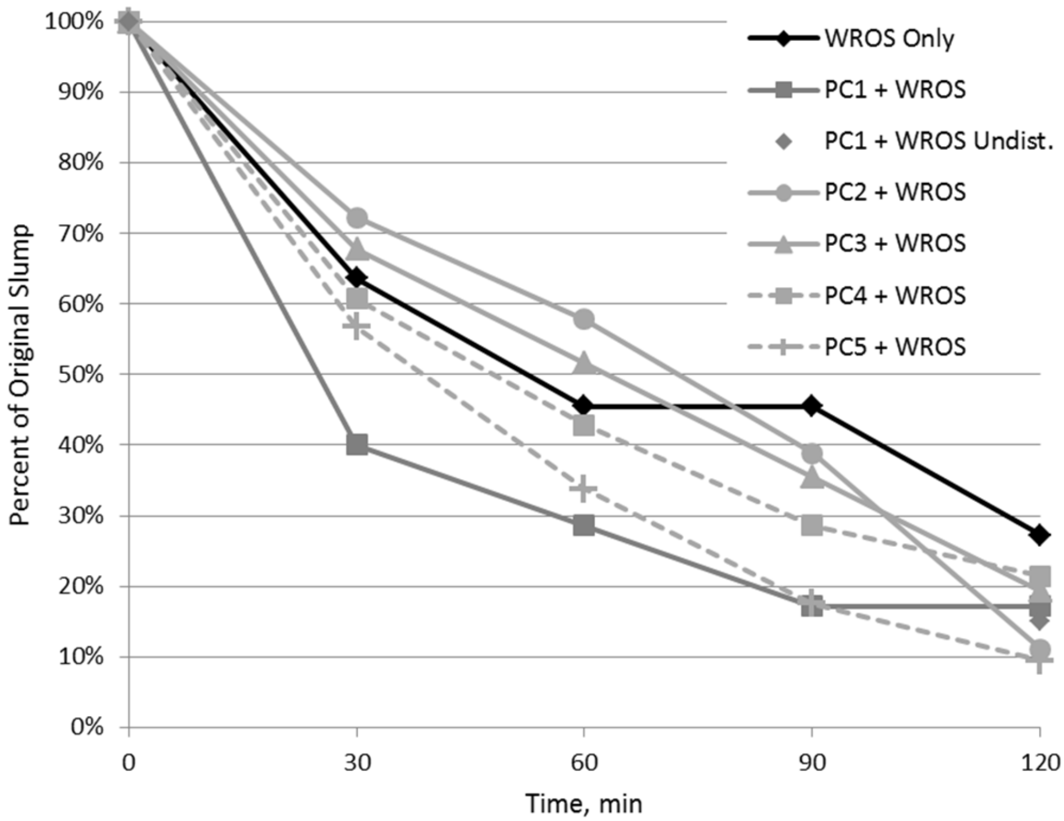

Figure 3. The changes of slump over time of select mixtures.

Figure 4 shows the changes in C231 air content over time for mixtures from Groups 1 and 3. Again, the mixtures not shown were omitted because they exhibited similar performance. The y-axis, which shows air content, is normalized to the initial measurement. Values plotted are percent of original air content versus the time of the measurement after mixing. The undisturbed mixture doesn't have its 0 and 120 minute points connected because values were not collected between those times. The points disconnected from the lines are the values from the modified C231 testing and correspond to the markers from the same mixtures. As can be seen, the air content in the samples consolidated immediately after mixing (modified C231) did not lose as much air as the samples that were allowed to sit statically for 120 minutes. This was consistent for all of the mixtures investigated. A comparison of all mixtures is made in Figure 5, which provides a comparison of each mixture's losses at 60 and 120 minutes of C231 air content, modified C231 air content, and slump, all normalized to their original values.

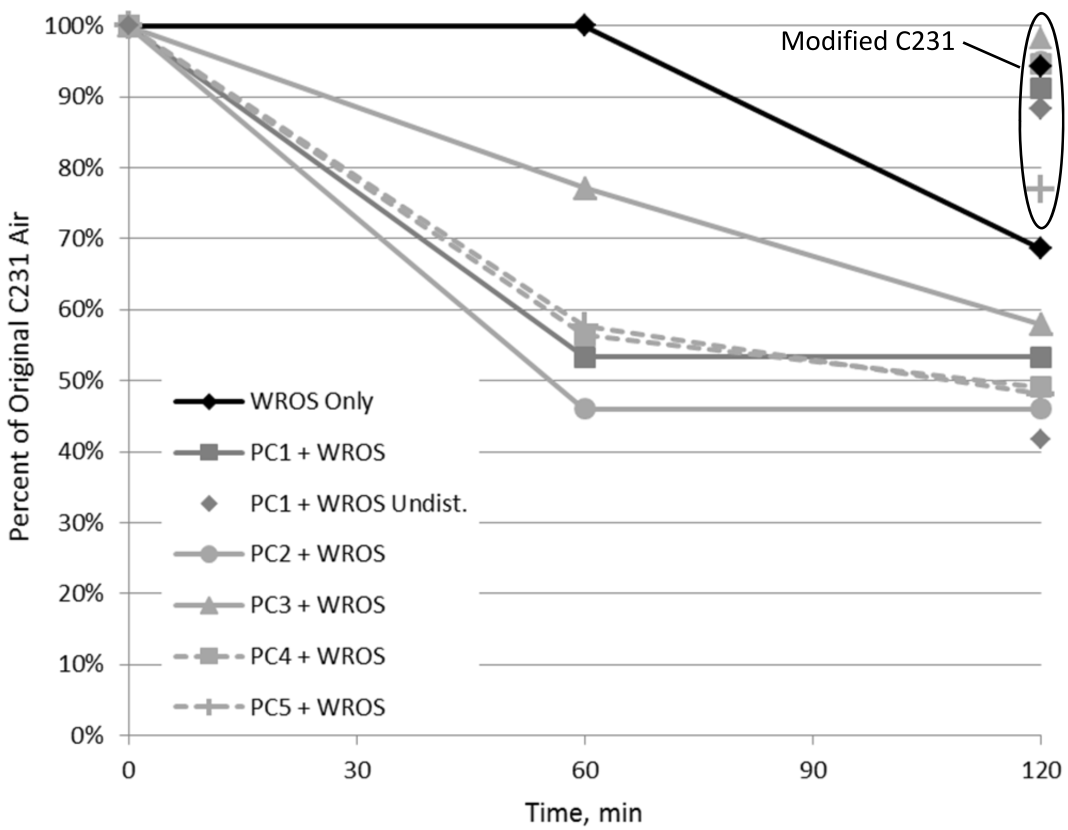

Figure 4. The changes of air content over time of select mixtures.

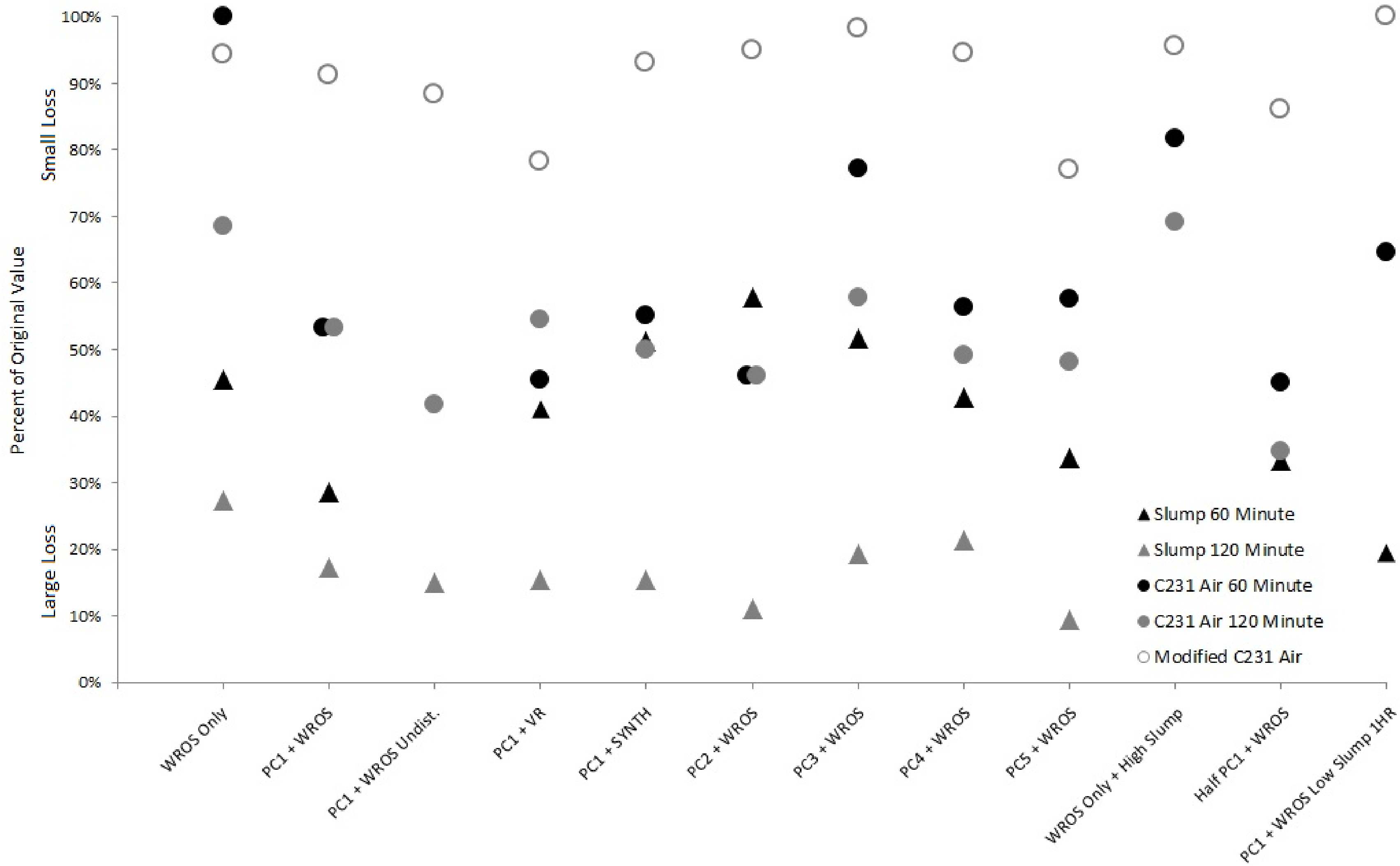

Figure 5. The normalized values of slump, air content, and modified air content at 60 and 120 minutes.

Figure 6 shows the air content as a function of the AEA dosage. The points are plotted only from data collected at 0 minutes. One specimen had an abnormally large AEA dosage and lies beyond the maximum x-axis value shown. This point is labeled with its x-value of 3.91 oz./cwt.

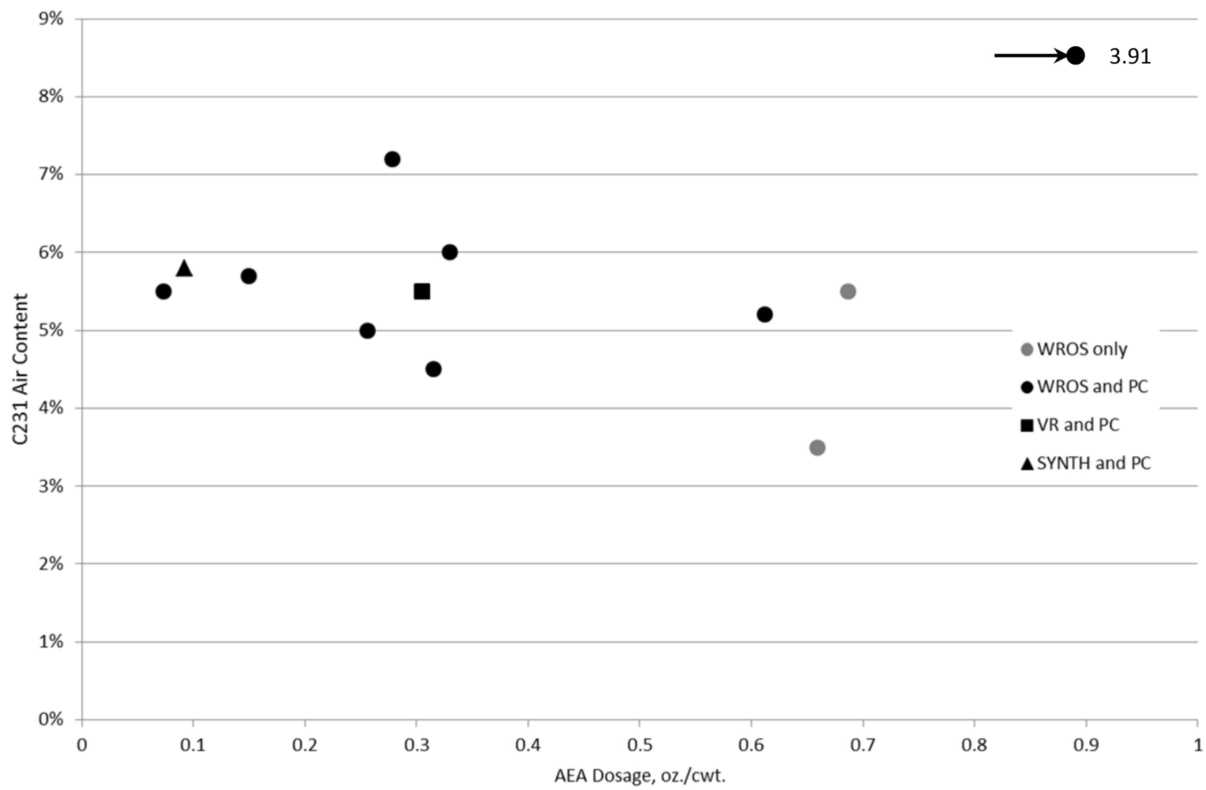

Figure 6. AEA dosage versus C231 air content at 0 minutes.

Figure 7 shows spacing factor as a function of C231 air content. All specimens tested for frost durability are shown. Specimens containing a PC are represented by a square, and specimens not containing a PC are shown with a circle. Those specimens which had a DF at or above 80% (passing) are represented by a solid shape, and those mixtures which failed testing, either with a DF below 80% or by becoming untestable at or before 300 cycles are represented by an open shape. Lines are drawn at spacing factors of 0.008 in. and 0.010 in. These are recommended maximum values from ACI 201 and CSA respectively. Trendlines are plotted for mixtures with and without a PC.

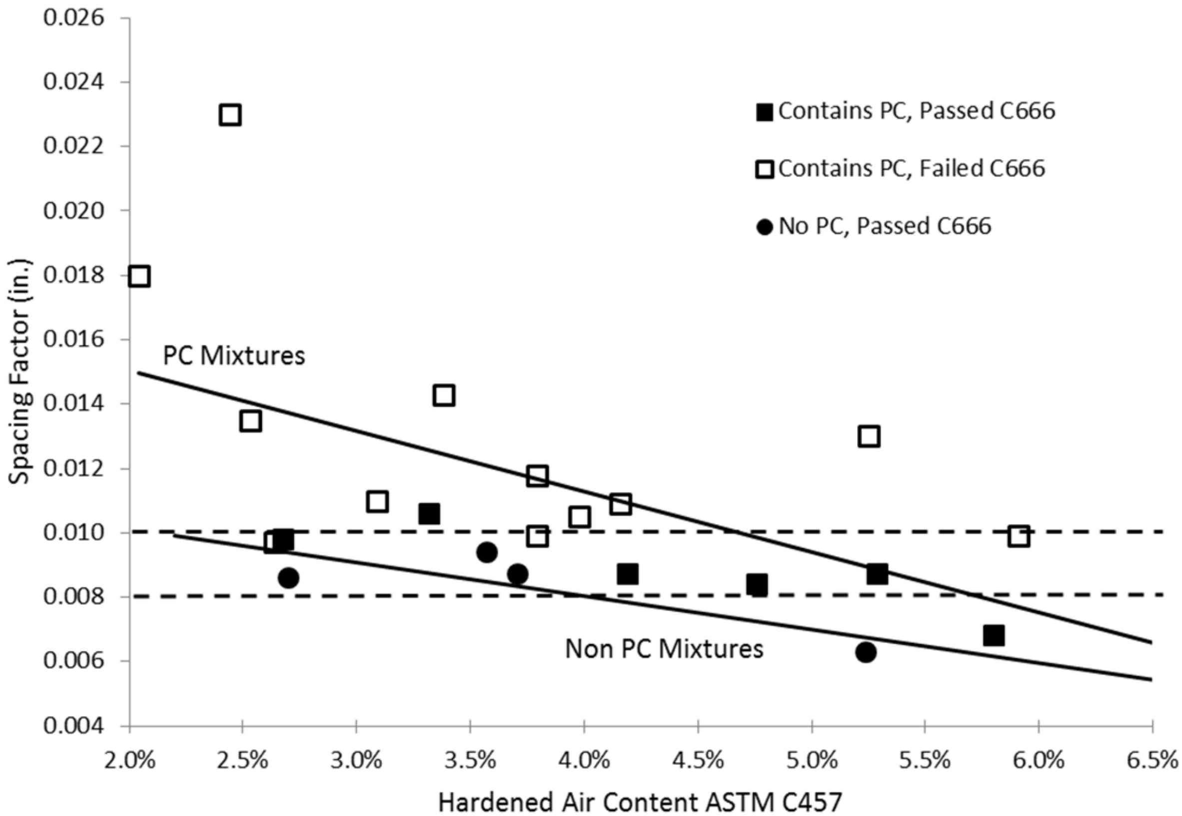

Figure 7. Spacing factor versus hardened air content for mixtures that were tested for freeze-thaw durability.

Figure 8 displays a normalized version of the air-void distribution. The y-axis shows chord frequency, which is normalized to 100% for each mixture, and the x-axis shows chord length in microns. Note that the ranges have been truncated at 300 microns for display purposes. Mixtures containing PC are shown in grey, while the mixture without PC is in black. Open points indicate the mixture failed C666 testing, while solid shapes indicate the mixture passed C666 with an acceptable DF.

Figures 9 and 10 represent the air-void distributions for the all the mixtures in this study at 0 and 60 minutes respectively. The y-axis shows the chords per inch for each mixture, normalized to the traverse length which was constant for all samples. The x-axis shows ranges of chord lengths in microns. Again, the ranges have been truncated at 300 microns. The mixtures are distinguished by whether or not they passed (black) or failed (grey) freeze-thaw testing and whether they contained PC (solid) or did not (dashed).

Figure 11 shows the air-void distribution of select mixtures at 0 minutes. The y-axis shows the air content fraction, which is normalized to 100% for each mixture, and the x-axis shows the chord length in microns, truncated at 300 microns for display purposes. As with Figures 9 and 10, the mixtures are distinguished by whether or not they passed (black) or failed (grey) freeze-thaw testing and whether they contained PC (solid) or did not (dashed).

Figure 12 shows the air-void distribution of two mixtures both at 0 and 60 minutes. The y-axis shows the air content fraction, which is normalized to 100% for both mixtures, and the x-axis shows the chord length in microns, truncated at 300 microns for display purposes. The 0 minute data is shown by the solid lines, and the 60 minute data is shown by the dashed lines.

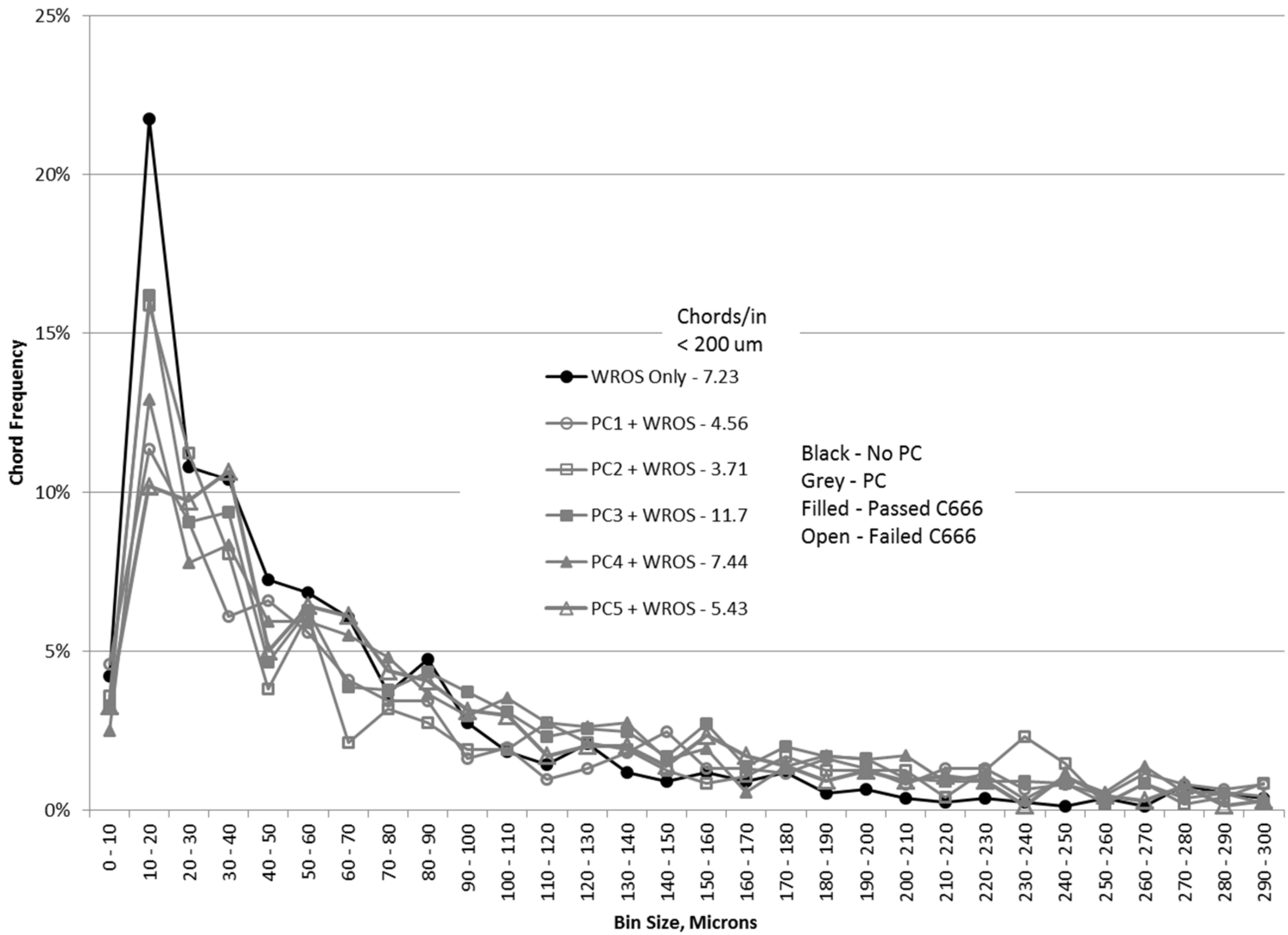

Figure 8. The hardened air-void distribution by chord frequency of select mixtures at 0 minutes.

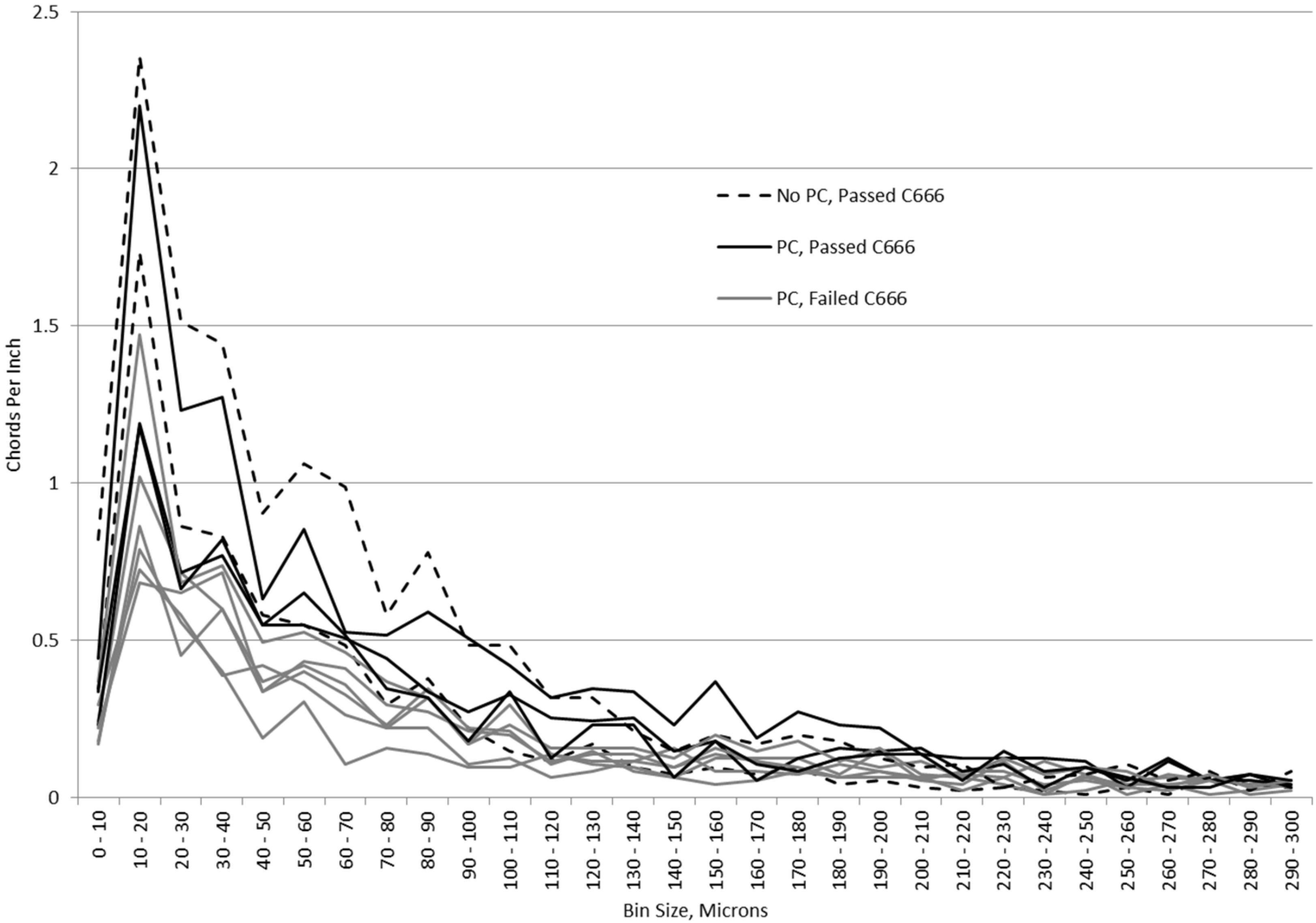

Figure 9. The hardened air-void distribution by chord count per inch of all mixtures at 0 minutes.

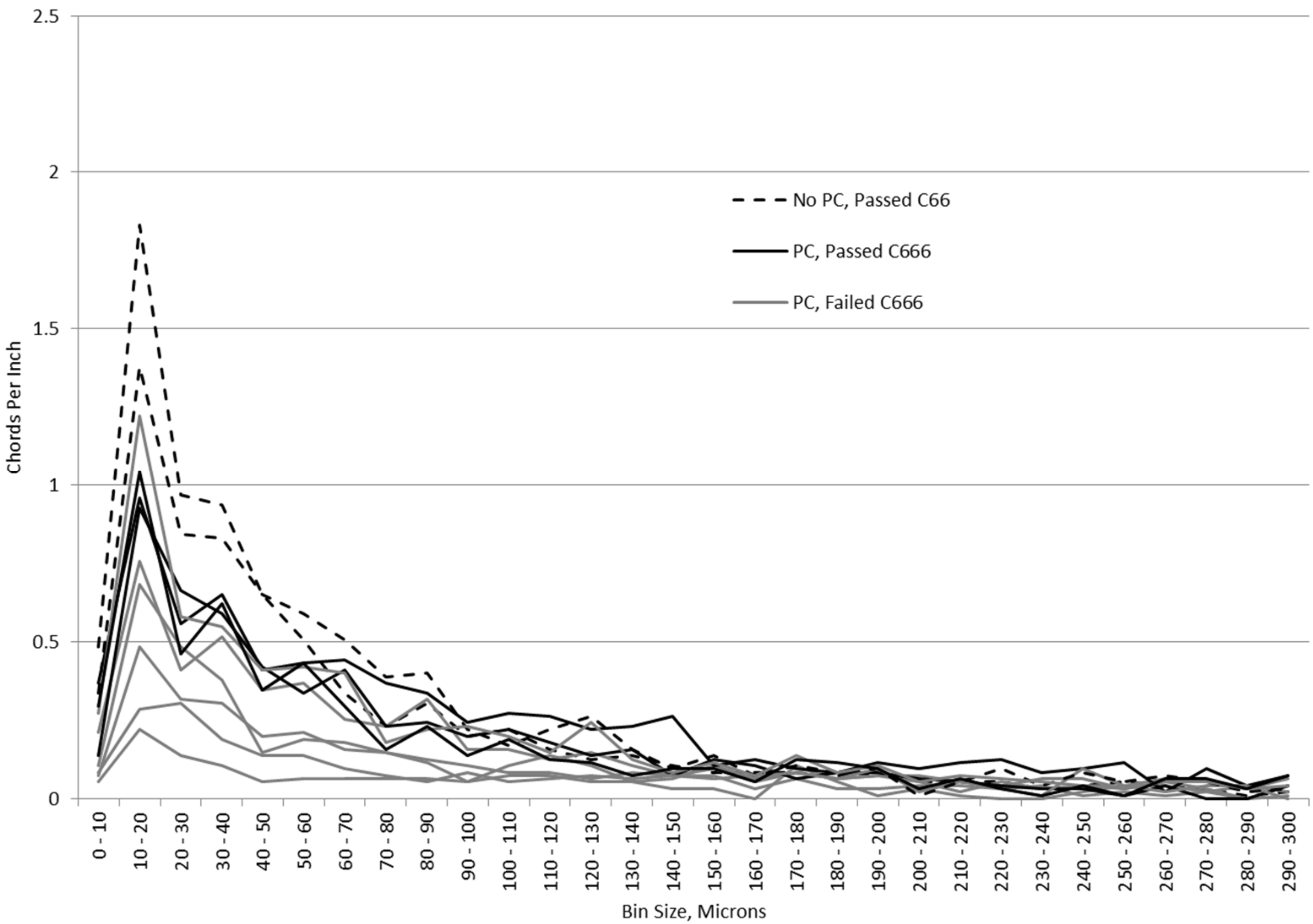

Figure 10. The hardened air-void distribution by chord count per inch of all mixtures at 60 minutes.

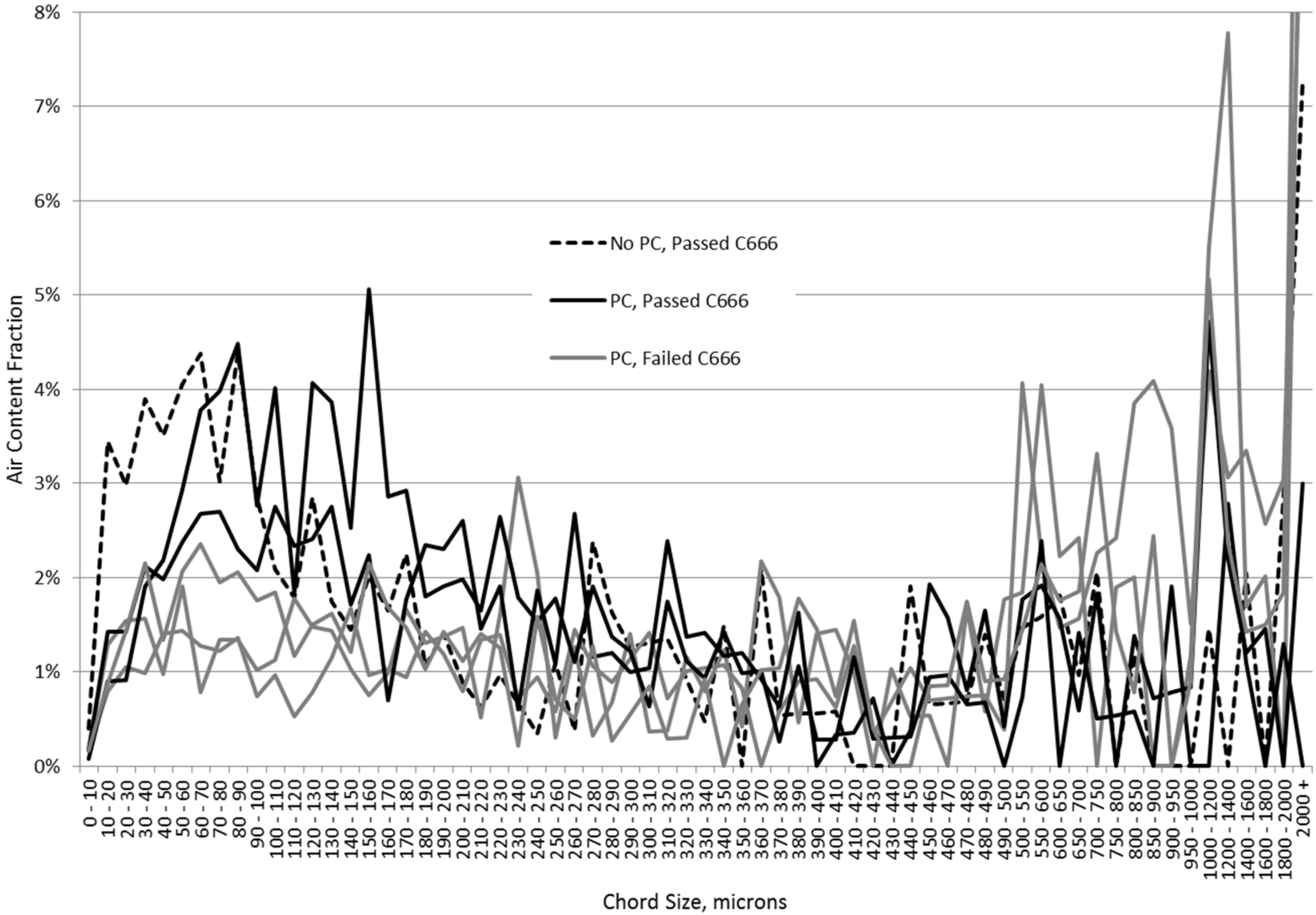

Figure 11. The hardened air-void distribution by normalized air content of select mixtures at 0 minutes.

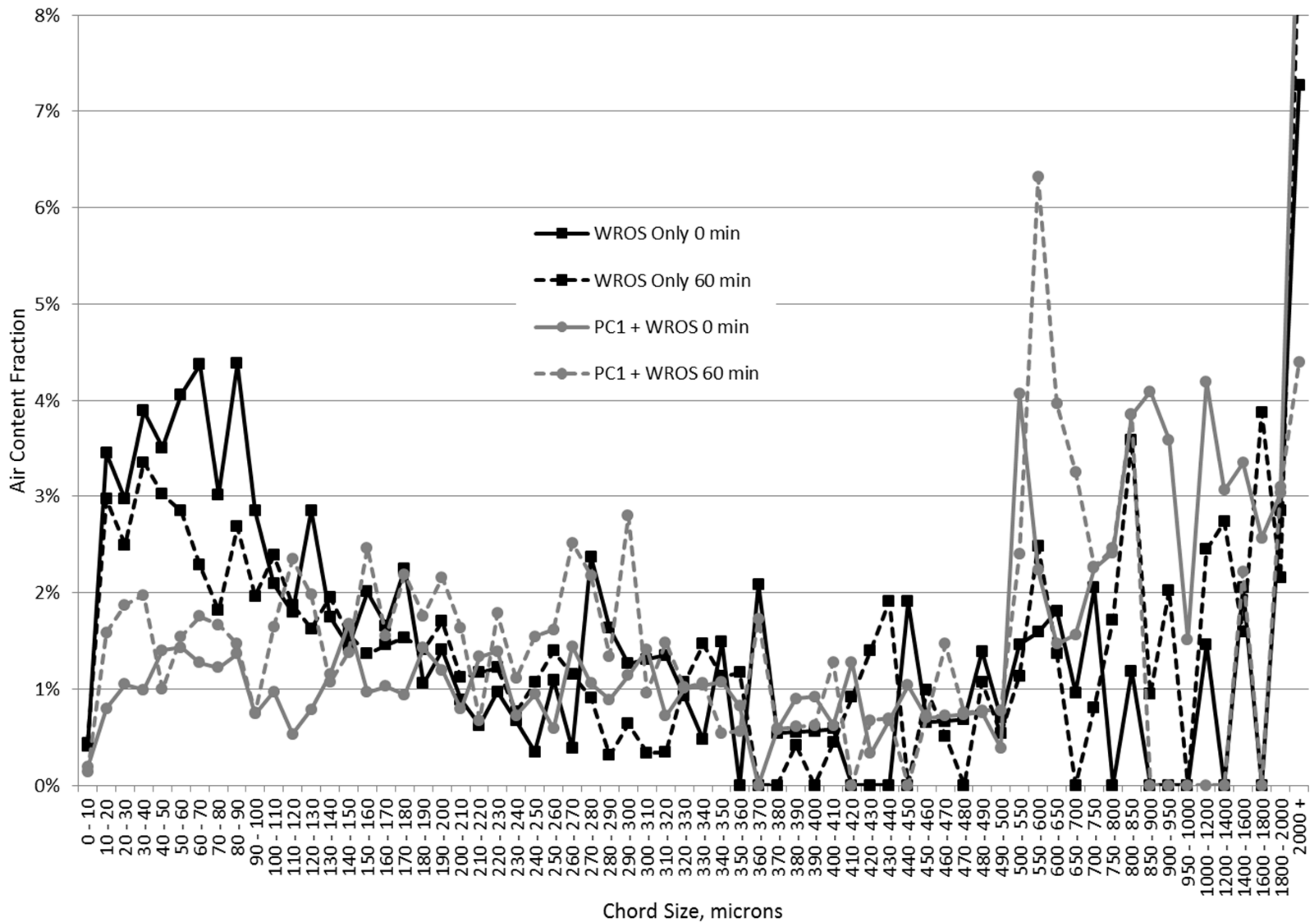

Figure 12. The change in the hardened air-void system of two mixtures from 0 to 60 minutes.

A useful method to investigate the data was found by looking at the number of chords between 0 and 200 microns. Table 9 shows the number of chords per inch in this range as well as the DF for each of the mixtures tested for freeze-thaw durability in this study.

Table 9. Chords per inch observed between 0 and 200 microns and DF for all mixtures.

Mixture ID	Time (min.)	Chords/in. < 200 µm	DF
WROS Only + High Slump	0	13.28	97 ± 3%
PC3 + WROS	0	11.7	97 ± 3%
WROS Only	60	7.61	97 ± 3%
WROS Only + High Slump	60	7.55	93%
PC4 + WROS	0	7.44	95.8%
WROS Only	0	7.23	97 ± 3%
Half PC1 + WROS	0	7.23	69 ± 5%
PC1 + WROS Low Slump 1HR	0	7.19	96.7%
PC3 + WROS	60	6.55	100%
Half PC1 + WROS	60	5.8	(300)
PC1 + VR	0	5.75	(190)
PC5 + WROS	0	5.43	(300)
PC4 + WROS	60	5.39	92 ± 2%
PC1 + SYNTH	0	5.16	(173)
PC1 + WROS Low Slump 1HR	60	5.14	86 ± 8%
PC1 + WROS	0	4.56	(137)
PC1 + SYNTH	60	4.55	(123)
PC2 + WROS	0	3.71	(105)
PC1 + WROS	60	3.34	(66)
PC5 + WROS	60	2.89	(240)
PC2 + WROS	60	2	(105)
PC1 + VR	60	1.36	(113)

Frost Durable

2.4 Discussion

2.4.1 Impact of Sampling on Test Results

The protocol used to measure air stability testing is a nonstandard testing procedure. This novel procedure was validated by the inclusion of the undisturbed mixture. The undisturbed mixture helped to validate that the stability testing, which included sampling over time from the bulk material, did not bias the results while sampling or the sample volume. Because the undisturbed mixture was only sampled once before 120 minutes, the amount of material remaining was still considerable. The measurements for this mixture agreed with the same mixture that was sampled over time, PC1 + WROS. Therefore, the testing method was considered valid, and neither the sampling throughout testing nor the remaining volume of material was determined to be an issue.

2.4.2 Stability of Slump and Air Content in Fresh Concrete

All mixtures in this study lost slump over the course of testing. The average slump loss was 55% at 60 minutes and 83% at 120 minutes. There were no strong trends in slump loss among any of the groups. The lack of difference among the groups indicates that the presence of superplasticizer, the choice superplasticizer or air-entrainer, and the mode of obtaining workability do not seem to change the percentage of slump loss over time.

While the slump loss was consistent among the mixtures, the air loss was not. As shown in Figure 4, the mixtures containing PCs lost more air than the mixture only containing wood rosin. In Group 4, the mixture containing only wood rosin with a 0.50 w/cm also shows a smaller loss in air content than the mixtures containing superplasticizer. This is shown in Table 8 and Figure 5. ***The average loss of air in the two mixtures containing only wood rosin was around 31%, but the average loss in mixtures containing superplasticizers was 50%. While the presence of PC seemed to have an effect on air loss, the choice of PC specifically did not have an observable impact, as all the different PCs performed similarly. Likewise, the choice of AEA also did not seem to make an individual impact.*** At 60 minutes, the average loss in air was 45% for mixtures containing PC and 32% for mixtures without. The mixture with the 0.37 w/cm, PC and a wood rosin only lost 35% of its air content, but this occurred in 60 minutes. It is possible that reducing the w/cm may reduce the loss of air over time in the bulk material, but more testing needs to be done to verify this. It is possible that the PC and defoamer may reduce the adhesion between the AEAs and cement grains and entrained voids shown in previous work by Ley et al. (2010). These points are discussed in more depth with the mechanisms of air loss.

2.4.3 Impact of Consolidation on the Stability of the Fresh Air Content

The modified pressure meter test was used to compare the changes which occurred in the unconsolidated bulk material with the changes that occurred in consolidated specimens. Parallel C231 specimens were prepared at 0 minutes but were tested at 120 minutes for all mixtures except one that was tested at 60 minutes because of early stiffening attributed to a low w/cm.

For mixtures containing only wood rosin, the average loss of air decreased from 31% to 5%. For mixtures containing superplasticizer, the average loss in air changed from 50% to around 10%. This suggests that the act of consolidation reduces the loss of air content over time. Consolidation brings all of the constituents in the mixture closer together and likely makes it more difficult for bubbles to escape from the mixture. It also removes large air pockets, effectively reducing the internal surface area which bubbles can escape through. If the presence of the PC is reducing the attraction between the entrained air-voids and the cement grains, the physical rearranging of material from consolidation may be compensating for the loss in attraction. ***This is an important finding as it suggests that consolidating the mixtures will reduce this air loss over time.***

2.4.4 Other Observations in Fresh Material

The dosage of AEA used in the mixtures containing PC was generally much lower than in mixtures containing only wood rosin, despite these mixtures having been calibrated to have the same 5% air content. The average dosage for mixtures not containing PC was 0.67 oz./cwt., producing an average of 4.5% fresh air content. In mixtures containing PC, the average dosage was 0.27 oz./cwt., giving an average air content of 5.6% air, disregarding the 0.37 w/cm mixture. This can be seen in Figure 6. One notable case is the mixture containing the synthetic AEA. This mixture only required 0.09 oz./cwt. of AEA to reach the target air content. Other work by the research team with the same admixture shows that without a PC, a dosage over 10 times higher would be needed to obtain a similar air content (Felice, 2012). This suggests that the PCs have a synergistic interaction with the AEAs, causing them to be more effective. This reduction in dosage likely means that less of the AEA is present at the surface of the voids. Again this strengthens the argument that there is less adhesion between voids and cement grains. This lower amount of AEA may also cause a change in the stabilized void distribution.

2.4.5 Hardened Air-void Analysis and Freeze-Thaw Durability

Figure 7 shows spacing factor as a function of fresh air content. A trendline is plotted for all the PC specimens and for all the non PC specimens. The point that a trendline intersects a given spacing factor shows an average air content needed to achieve that spacing factor for either PC or non PC mixtures. The trendline for PC mixtures has a considerable offset to the right from the non PC mixtures. This means that in order to achieve a given spacing factor, a higher volume of air is needed in a mixture containing PC. Likewise, at a given air content, a mixture containing PC will have a larger spacing factor than a mixture containing no PC. This suggests that the inclusion of PC coarsens the air-void system, causing there to be a higher frequency of large voids and a lower spacing factor for a given volume. Hardened air-void analysis provides values for spacing factor and specific surface area, as well as void size frequency. As mentioned previously, ACI 201 recommends a spacing factor of at most 0.008 in., a specific surface area of at least 600 in.$^{-1}$, and, based on the maximum nominal aggregate size used in this study, 5 – 6% fresh air depending on exposure conditions.

In Group 1, the mixture containing only wood rosin had a spacing factor close to 0.008 in., but only had 3.5% air, and was still able to achieve an average DF of 97%. The mixture containing PC1 had a higher air content at 0 minutes of 5.3%, but also had a larger spacing factor of 0.013 in. and failed C666 in just 137 cycles. One explanation for the failing performance with the PC with the higher air content is the increased spacing factor. Another factor that can be considered is the actual size distribution of voids in these mixtures. Figures 9 and 10 show the number of chords per inch of traverse for each mixture at 0 and 60 minutes respectively. Figure 11 shows the normalized air content distribution of selected mixtures. It is clear in these figures that the mixtures passing C666 (black) have a higher number of small voids than the failing (grey) mixtures. Figures 9 and 10 show that passing mixtures contain more small voids; Figure 11 shows that passing mixtures have relatively more air volume in smaller voids and failing mixtures have more air volume in larger voids. The size range where this is most pronounced is up to 200 microns, after which void frequency becomes very low for any given size or mixture. This is quantified in Table 9, where each mixture is listed with the number of voids per inch smaller than 200 microns, as well as their freeze-thaw results. As the table shows, all mixtures with more than 6 voids per inch smaller than 200 microns passed C666, with only one exception. The 0 minute specimen with a half dosage of PC1 completed testing with a failing DF of 69 ± 5%, and it had 7.23 voids per inch. This is the only specimen to complete testing but have a DF below 80%. No specimens with fewer than 5 voids/in. passed C666. This measurement helps to quantify the quality of a specimen's air-void system, along with spacing factor and specific surface area.

In Group 2, all three mixtures failed C666 testing. This is expected based on the hardened air parameters. All three mixtures had spacing factors of 0.0109 in. or higher, specific surface areas less than 600 in.$^{-1}$, and fewer than 6 voids per inch smaller than 200 microns. The synthetic AEA produced the lowest spacing factor and the highest specific surface area among the three mixtures. Its system also had the smallest changes from 0 to 60 minutes. Despite having the smallest AEA dosage by a significant margin, the synthetic AEA therefore produced the most stable system over time. More work is needed to better understand the synergistic effects of the PC and the synthetic AEA. The vinsol resin showed the most dramatic change. Its spacing factor nearly doubled between 0 and 60 minutes, and its specific surface area reduced by almost 38%. The vinsol resin and the synthetic AEA mixtures had similar air contents at 0 minutes, but the vinsol resin had a lower content at 60 minutes. Despite its air content decreasing, the wood rosin mixture did not see much change in spacing factor. Its specific surface area actually increased over time. Overall the different AEAs did perform differently, but they all failed to produce a frost durable air system when paired with PC1 at the air contents investigated.

In Group 3, PCs 1, 2, and 5 failed C666 testing and PCs 3 and 4 passed. The mixture containing PC2 produced the worst air system in the group, and it would be expected to fail based on the above discussion on all parameters. The mixture containing PC5 had marginal values for spacing factors (0.0099 and 0.0097 in.) and specific surface areas (559 and 581 in.$^{-1}$). The void count for the 0 minute specimen was also marginal (5.43 voids/in.) and poor at 60 minutes (2.89 voids/in.). However, the mixtures containing PC3 and PC4 produced satisfactory air systems within the recommended parameters. The difference in performance is likely dependent on the specific chemical makeup of each PC and their different components. All the systems exhibited similarly small changes over time. While more work is needed, this implies that the stability of the air systems is likely based on the AEA, while the quality of the air system seems to be controlled more by the chosen PC.

In Group 4, the mixtures containing PC at 0.45 w/cm both failed C666, and the two mixtures without PC and the PC mixture with a w/cm of 0.37 all passed. The mixture containing a half dosage of PC1 had the most borderline C666 performance in the study. While most mixtures had a similar outcome at 0 and 60 minutes, this mixture completed testing at 0 minutes with a failing DF but terminated testing at 60 minutes at 300 cycles. Klieger (1952, 1956) has shown that the progression of damage due to freeze-thaw cycling is rapid once durability begins to decline. This can explain how the mixture could perform the way it did in C666 testing. Its 0 minute sample had borderline acceptable spacing factor of 0.0099 in., a low specific surface area of 453 in.$^{-1}$, and a high void count of 7.23 voids/in. smaller than 200 microns. It should be noted that the fresh air content was much higher than usual at 7.2%. ***This specimen shows that it is possible to achieve a frost durable concrete with this combination of admixtures with a high enough air content.*** The 60 minute sample had a slightly worse system and would more easily be predicted to fail C666 testing. The mixture with the 0.50 w/cm produced both a great air-void system and great C666 performance. This furthers the notion that the problems produced with the PC mixtures are based on chemistry and not simply the increase in workability of the mixture. The mixture containing PC1 and a 0.37 w/cm ratio had good parameters and performance at 0 minutes, but it should be noted that the mixture had a high air content at 8.5%. The 60 minute specimen had marginal values for spacing factor and specific surface area and the lowest void count for any specimen that passed C666. It also had a high variability between C666 specimens, but it did pass. This mixture provides an interesting point to examine in the data set. A suitable air system could be a result of the higher air content alone, but it is possible that the reduction in w/cm helped to stabilize the voids in the mixture. Reducing the w/cm would cause the constituents of the mixture to ultimately be closer together, similar to the change produced from consolidating versus not consolidating. This could allow for a better air system in the hardened mixture. The fresh air content might be locked in by consolidation, but the relative size and position of voids might still change over time, based on the changes in the hardened air-void parameters over time. There is currently no established way to measure these parameters in fresh material. However, if changes do occur after consolidation that weaken the overall quality of the air system, it is possible that a lower w/cm reduces these changes.

2.4.6 Changes to the Void System Over Time and Possible Mechanisms

It is evident that the mixtures lose air over time. The shapes of Figures 9 and 10 can be compared to analyze which voids are being lost over time. The distributions at 0 and 60 minutes have very similar shapes. Figure 12 can be used to see that, for the mixtures shown, the air content is the same for each void size at 0 and 60 minutes. ***The loss in air is occurring uniformly across all void sizes.***

It has been shown by Ley et al. (2010) that there is a strong adhesion between cement grains and the surface of an entrained void. It is well known that PCs repel cement grains due to steric hindrance of free water (Ramachandran 1995). It is possible that this repulsion interferes with the adhesion to the air-entrained surface of the voids in the material. This would reduce the stability of the voids in the system by allowing them to escape to free surfaces. These surfaces could be at the top of the concrete or within larger voids in the concrete. If the mechanism of air loss is the evacuation of voids at an exposed surface or within larger voids, it stands to reason that consolidation would reduce this effect. ***Consolidation brings all constituents in the material closer together, and it removes large air pockets from the mixture, reducing the internal surface area. This would both serve to restrain the air-voids and reduce the number of sites where they could escape.***

Without intimate knowledge of the materials and formulations used to produce commercial PCs, it is challenging to understand the synergistic effects of the PC, AEA, defoamer, and cement. The simultaneous creation, reduction, and stabilization of bubbles during the mixing of the concrete is a complicated phenomenon. However, it appears that air-entrained concrete mixtures with a PC and defoamer do not create void systems of the same quality or stability as mixtures with just AEA. Much fundamental work is needed to understand and ultimately shape these interactions to minimize the loss of voids over time and improve the quality of the stabilized void system.

2.4.7 Practical Implications

The use of PCs as superplasticizers in concrete is a powerful tool that can improve strength, economy, sustainability, and durability of concrete mixtures. This is a tool that the industry cannot lose. However, this study highlights challenges with stability and void system quality of PCs. All concrete in this study was produced in a laboratory drum mixer. One should be careful if directly extrapolating the data in this paper to field concrete without first understanding the changes the mixing energy may cause. Based on the author's experience, these void systems should have higher percentages of small voids for a given volume of air produced; however, no data has been published in this area. Also, all concretes investigated were allowed to sit undisturbed in a wheelbarrow between sampling periods and the concrete was not agitated before it was sampled. The loss of air and change in quality of the air-void system is likely less conservative than what occurs under mild agitation during the transportation of the concrete.

In addition to highlighting the challenges with these materials, this paper also gives tools to manage these challenges. Based on the modified C231 tests, it is clear that consolidating a concrete mixture as soon as possible after placement will minimize the loss of air over time. This was observed in mixtures with and without PCs. Because of the changes that do occur between mixing and consolidating, mixtures should be measured for fresh properties just before consolidation and not sooner for quality control. When using PC based superplasticizers, a higher air content may be necessary to achieve frost durability because of the coarsening of the air-void system. The air contents required in these mixtures are higher than current recommendations in ACI 318, which are based on work completed by Klieger with only Vinsol resin AEA (1952, 1956). The current code requirements should be reexamined for these new materials. However, frost durable mixtures can be provided if enough small voids are provided in the concrete. This would likely be obtained by increasing the overall volume of the air required in the mixture.

It should also be noted that ASTM C666 is a harsh test that may not replicate all combinations of moisture and subsequent temperature changes that occur in the field. However, this test is recognized by ASTM C260, C494, and C1017 as being a useful test to evaluate frost durability. Again care should be taken before extrapolating the laboratory data presented to field applications.

2.5 Conclusion

In this study, concrete mixtures were prepared to compare the effects of PCs on the stability, quality, and frost durability of the air-void systems created by air-entraining agents. Variables examined include the presence of five PCs and three different popular AEAs and different w/cm. Based on the data collected, the following observations have been made for the mixtures and materials in this study:

- Slump and air decrease over time in unconsolidated concrete for all mixtures investigated.
- The slump loss was similar in all mixtures on a percent basis.
- The inclusion of PC caused greater loss in air over time.
- Consolidation drastically reduces the loss in air, both with and without a PC.
- PCs appear to reduce the adhesion between cement grains and the entrained air-voids.
- PC1, 2, and 5 coarsen the air-void system, causing the total volume of air in the mixture to be comprised of larger voids.
- Because of this coarsening, some PC mixtures require a higher air content to achieve ACI 201 recommended values for spacing factor and specific surface area and for frost durability as per ASTM C666 under limits defined in this paper.
- For a given PC, the choice of AEA affects the stability of the air-void system over time.
- For a given AEA, the choice of PC affects the overall quality of the air system.
- In a mixture containing PC, either reducing the w/cm or the dosage of PC improves the quality of the air system and therefore rapid freeze-thaw performance.
- For the mixtures examined in this study, the following values were adequate for frost durability:

- A maximum spacing factor of 0.0094 in.
- A minimum specific surface area of 600 in.$^{-1}$
- A minimum of 6 voids/in. smaller than 200 microns

This study provides observations that need to be more thoroughly investigated. Additional work needs to be done to understand the interactions between AEAs and PC with a wider amount of materials. This study could easily be expanded to provide more data on the interaction of various AEAs with other PCs, the effect of the dosage of PC, impact of cement type, and the effect of the w/cm. Further study should also pinpoint the interaction of defoaming agents with AEAs and their effect on the air-void system quality.

Chapter 3: Conclusions

This thesis presents a study of modern concrete containing Polycarboxylate (PC) superplasticizers and various air-entraining agents (AEAs) used in industry. The study includes various combinations of PCs, AEAs, and w/cm's. Mixtures were tested for slump (ASTM C143), unit weight (ASTM C138), and fresh air content (ASTM C231). A novel testing method was employed to examine the effect of consolidation over time on air content. This modified C231 method was performed by preparing a second C231 sample with the first and testing it for air content after 120 minutes had elapsed. Mixtures were also tested for rapid freeze-thaw durability (ASTM C666) and were analyzed for hardened air-void properties (ASTM C457). Following the investigation, the following conclusions were found:

- Slump and air decrease over time in unconsolidated concrete in all mixtures investigated and the slump loss was similar in all mixtures on a percent basis
- The inclusion of PC caused greater loss in air over time
- Consolidation drastically reduces the loss in air, both with and without a PC
- PCs appear to reduce the adhesion between cement grains and the entrained air-voids
- PC 1, 2, and 5 coarsen the air-void system, causing the total volume of air in the mixture to be comprised of larger voids.

- Because of this coarsening, some PC mixtures require a higher air content to achieve ACI 201 recommended values for spacing factor and specific surface area and for frost durability as per ASTM C666 under limits defined in this paper
- For a given PC, the choice of AEA affects the stability of the air-void system over time
- For a given AEA, the choice of PC affects the overall quality of the air system.
- In a mixture containing PC, either reducing the w/cm or the dosage of PC improves the quality of the air system and therefore rapid freeze-thaw performance.
- For the mixtures examined in this study, the following values were adequate for frost durability:
    - A maximum spacing factor of 0.0094 in.
    - A minimum specific surface area of 600 $in.^{-1}$
    - A minimum of 6 voids/in. smaller than 200 microns

Future work based on this study is suggested by the results collected. This work could include exploring the interaction between AEAs and PCs, including more admixtures and combinations thereof. The dosage of these admixtures, especially the PCs, would also need further examination. This study only employed one type of cement and included no pozzolans or cement replacements. Therefore future work could include these substitutions. Work should also be done to determine the appropriate volume of air that PC mixtures require to achieve a satisfactory hardened air system and frost durability. Additionally, correlations to field concrete would strengthen this paper’s major points. Static concrete from this study should also be compared to concrete idling in mixing trucks.

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