Class F Fly Ash Assessment for Use in Concrete Pavements

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WisDOT ID no. 0092-15-10

January 2017

WISCONSIN DEPARTMENT OF TRANSPORTATION
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Technical Report Documentation Page

1. Report No. WHRP 0092-15-10	2. Government Accession No	3. Recipient's Catalog No

4. Title and Subtitle Class F Fly Ash Assessment for Use in Concrete Pavements	5. Report Date January 2017 6. Performing Organization Code Wisconsin Highway Research Program
7. Authors Konstantin Sobolev, Mohamadreza Moini, Rani Pradoto, Marina Kozhukhova Ismael Flores-Vivian, Scott Muzenski, Habib Tabatabai, Hani H Titi	8. Performing Organization Report No. CBU-ZZ16-236-07
9. Performing Organization Name and Address UW-Milwaukee 3200 N Cramer St, EMS Milwaukee WI, 53211	10. Work Unit No. (TRAIS) 11. Contract or Grant No. WisDOT SPR# 0092-15-10
12. Sponsoring Agency Name and Address Wisconsin Department of Transportation Research & Library Unit 4802 Sheboygan Ave. Rm 104 Madison, WI 53707	13. Type of Report and Period Covered Final Report 2012-2015 14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The Wisconsin Department of Transportation (WisDOT) currently specifies Class C fly ash for use as a partial replacement for portland cement in concrete pavements. Class F fly ash sources were eliminated from WisDOT specifications in the 1990's due to high values of loss on ignition (LOI) which led to difficulties in establishing and maintaining a proper entrained air void system in the concrete used in paving applications. A recent study that looked at the use of Class F fly ash demonstrated its potential usage in WisDOT specifications.

However, WisDOT needs more evaluation with regard to durability testing. Specifically, research is needed to evaluate the feasibility of expanding current specifications to allow for use of Class F fly ash in concrete paving applications with southern Wisconsin aggregates. In order for Class F fly ash to be a viable alternative as a supplemental cementitious material, its use must produce mixes that meet current performance standards with respect to strength (including early strength) and durability, when compared with a commonly used Class C fly ash.

The main objective of this study is to evaluate whether the locally available Class F fly ash from Elm Road Generating Station, operated by WE Energies and located in Oak Creek, Wisconsin, will provide satisfactory performance in concrete pavement, in comparison with a Class C fly ash from Columbia Energy Center currently in use. The study will also provide mix design guidance related to acceptable proportions of Class F fly ash that can be used in paving applications without negatively impacting performance.

The performance evaluation of optimized concrete included workability (slump), air content, compressive strength, freeze-thaw and salt scaling resistance in accordance with the relevant AASHTO or ASTM standards. Finally, the reported research recommended the selection of fly ash for low-slump concrete with reduced cementitious material content intended for paving applications.

17. Key Words Fly ash, low cement concrete, admixtures, superplasticizer, supplementary cementitious materials, compressive strength, durability	18. Distribution Statement No restriction. This document is available to the public through the National Technical Information Service 5285 Port Royal Road Springfield VA 22161

18. Security classif.(of this report) Unclassified	19. Security classif. (of this page) Unclassified	20. No. of Pages 59	21. Price

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EXECUTIVE SUMMARY

Other than water, portland cement concrete is the most used commodity in the world. Major parts of civil and transportation infrastructure, including bridges, roadway pavements, dams, and buildings are made of concrete. Because of wide-scale applications of these structures in different climatic zones and associated exposures, concrete durability and long term performance are often of major concern. In 2013, the study of American Society of Civil Engineers (ASCE) estimated that one-third of America's major roads are in poor or mediocre condition [1]. The same article reports that annual investments of $170 billion on roads and $20.5 billion for bridges are needed to substantially improve the condition of infrastructure. In addition to durability concerns, the production of portland cement is associated with the emissions of approximately one ton of carbon dioxide per ton of cement (plus NO_x and SO_x). Therefore, replacement of portland cement with supplementary cementitious materials (SCM) is an important trend to reduce the emissions and to improve the sustainability of concrete. Indeed, the consideration of these issues as well as proper and systematic design of concrete intended for highway applications is of extreme importance as concrete pavements represent up to 60% of interstate highway systems with heavier traffic loads and severe exposure.

The combined principles of material science and engineering can provide adequate methods and tools to facilitate the improvements to concrete design and existing specifications. Critically, durability and enhancement of long-term performance must be addressed at the design stage. Concrete used in highway pavement applications has relatively low cement content and also can be placed at low slump. However, further reduction of cement (cementitious material) content to 280 kg/m^3 (470 lb/yd^3) — vs.

current specifications which require the use of 315 - 340 kg/m^3 (531 – 573 lb/yd^3) of cementitious materials for concrete intended for pavement applications and 335 kg/m^3 (21 lb/yd^3) for bridge substructure and superstructure—needs a delicate proportioning of the mixture to maintain the expected workability, overall performance, and to ensure long-term durability in the field. Such design includes, but is not limited to the optimization of aggregates and improvement of efficiency of supplementary cementitious materials (SCM), as well as fine-tuning of the type and dosage of chemical and air-entraining admixtures.

This research evaluated the performance of Class F fly ash concrete with cementitious material content to 280 kg/m^3 (470 lb/yd^3), which can be attractive for the design of sustainable concrete pavements. The combination of fly ash (Class C and/or F), chemical (mid-range and high range water reducing) admixtures and air-entraining admixtures were selected to comply with existing WisDOT concrete specification. The developed concrete mixtures were evaluated for fresh properties, compressive strength ranging from 1 and up to 28 days and also for important durability indicators such as freeze-thaw and salt-scaling resistance. The methods and tools discussed in this research are applicable, but not limited to a wide range of concrete used for civil and transportation infrastructure.

This research demonstrated a modern approach to incorporate up to 30% of Class F and C fly ash including a Class C and F fly ash combination in concrete with state of the art superplasticizers based on polycarboxylate ether (PCE).

The effective use of fly ash as partial replacement of portland cement is a very important strategy to reduce the environmental impact and improve the sustainability of

conventional concrete. Based on the established correlations, it was concluded that Class F fly ash can provide an adequate performance of concrete especially when used at cement replacement level of up to 15% in combination with superplasticizer. The optimized superplasticized concrete with Class C fly ash (used as a reference) demonstrated a very exceptional workability and mechanical performance.

ACKNOWLEDGMENTS

The authors would like to thank the Wisconsin Highway Research Program for sponsoring this research. The authors would also like to thank Lafarge Cement Company, Holcim US Inc., We Energies Corporation, American Materials, Zignego Ready Mix, Handy Chemicals, BASF Chemical Company, W. R. Grace Company and Waste Hub for providing all materials required for the project.

The authors would like to convey special thanks to all students and lab personnel who assisted in preparation of concrete mixtures, tests and heavy work in the lab: Clayton Cloutier, Nathaniel Havener, Katie LeDoux, Andrew Sinko, Leif Stevens Jackson, Emily Ann Szamocki, and Rahim Reshadi.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

The Wisconsin Department of Transportation (WisDOT) currently specifies Class C fly ash as a partial replacement for portland cement in concrete pavements. Class F fly ash sources were eliminated from WisDOT paving materials specifications in the 1990's due to high values of loss on ignition (LOI) which led to difficulties in establishing and maintaining a proper entrained air void system in the concrete. A recent WHRP study 0092-13-04 had demonstrated a potential applicability of Class F fly ash in WisDOT projects and revealed some limitations of this material.

One of the modern trends in infrastructure development is related to the application of concrete with supplementary cementitious materials (SCM). The use of SCM, including industrial by-products such as ground granulated blast furnace slag (GGBFS, also known as slag cement) and fly ash, can reduce the consumption of portland cement by up to 50% and 30%, respectively, as well as can enhance the workability, mechanical properties, durability performance, service life, and other characteristics of concrete. One of the well investigated SCM is fly ash, a by-product from power generation plants [2]. Many researchers have investigated the effects of fly ash as supplementary cementitious materials (SCM) [3-5]. Fly ash has been widely used in concrete technology for cement replacement since the 1930s, helping to reduce the cost of concrete and environmental problems associated with fly ash landfilling. There are two types of fly ash used in concrete: low-calcium fly ash (ASTM Class F) and high-calcium fly ash (ASTM Class C). Fly ash Class F (AF) is typically produced by burning of anthracite or bituminous coal and generally is an effective pozzolanic material consisting of silicate glass modified with aluminum and iron. At the same time, Class C fly ash (AC) is produced by burning of lignite or sub-bituminous coal. Class C fly ash contains a higher content of lime, more than 10%. Fly ash suitable for concrete applications is defined by ASTM 618, and its classification is based on the total quantity of SiO_2, Al_2O_3, and Fe_2O_3.

Fly ash can be defined as fine material based on aluminosiliceous, ferric oxide (Fe_2O_3) and calcium oxide (CaO) compounds that may also contain carbon and other metallic oxides as impurities. Class F fly ash is a pozzolanic material containing siliceous or aluminosiliceous components in a finely divided form that can react with calcium hydroxyde to form calcium silicate hydrates and other cementitious compounds. The size of fly ash varies from less than 1 µm to more than 100 µm with typical average size under 20 µm. The shape of fly ash particles is represented by solid spheres and hollow cenospheres. The surface area is within the range of 300 to 500 m^2/kg. Finer fly ash material considerably improves the mechanical properties of concrete without reducing the workability.

The chemical and physical properties of fly ash are defined by the requirements of ASTM Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for use in concrete (C618). As a replacement for portland cement, up to 30% of fly ash can be used as an SCM. There are many advantages to using fly ash as a replacement for portland cement [1-6]:

- Improved ultimate compressive strength;
- Increased resistance to alkali silica reaction;
- Increased resistance to sulfate attack;
- Reduced heat of hydration ;
- Reduced porosity and permeability;
- Reduced water demand;
- Improved workability;
- Reduced cost.

Blending SCM such as slag cement with portland cement, results in chemical activation and provides excellent long-term cementitious properties. Pozzolanic by-products (especially Class F fly ash) can react with $Ca(OH)_2$ released due to cement hydration, resulting in the formation of an additional C-S-H, increasing the volumes of the main binding component in the hydrating matrix. Also, pozzolanic fly ash can combine with cement alkalis (K_2O and Na_2O), minimizing the risk of an alkali-silica reaction.

To date, numerous research projects have been conducted on the application of fly ash as a pozzolanic material focusing on strength development and densified structure of cement-based composites. The most important parameters affecting the performance of fly ash are calcium content and particle size distribution. Ultra-fine particles can provide a nucleation effect initiating and accelerating the hydration of cement. Celik et. al reported that the finer particles of fly ash can be used to achieve higher compressive strength [6]. This work established the relationship between particle size distribution and compressive strength. Additionally, the microstructural investigation was conducted for fly ash samples revealing the shape and size differences and, thus, the potential effects on the compressive strength. As a result, ASTM-grade fly ash products were specified as a replacement for portland cement at up to 30%; however, at higher substitution rates, a decrease in strength was observed.

The incorporation of fly ash can affect the early strength development of concrete. The heat of hydration, strength development and setting times may be delayed, especially, at high volume replacements. Thongsanitgarn et. al [7] investigated the effect of fly ash on heat of hydration in blended cements and high calcium fly ash incorporated with limestone powder. The heat of hydration was accelerated vs. the reference blend of fly ash and portland cement and strength increased due to the contribution of finer limestone particles (with the size of 5 µm). It was proposed that finer particles have a greater surface area enabling the increase of nucleation site density accelerating the hydration. Additional results indicated the stabilization of ettringite at the age of 28 days when both limestone and fly ash were applied. Furthermore, to overcome a poor early age strength development, the mechanical activation of fly ash was proposed [8]. Fly ash mainly consists of amorphous material, and thus the activation carried out by mechanical milling can improve the reactivity. The main objective of using milling was to reduce the size of cement and SCM particles. A new nano-cement concept with mechano-chemical activation, accelerated hydration and the formation of nano-cement and nano C-S-H was proposed by Sobolev et al [9]. It was concluded that the activated cement produced with mechano-chemical activation (MCA) can provide significantly improved strength at all ages of hardening.

The use of industrial by-products (IBP) as mineral additives or supplementary cementitious materials (SCM) comprises a valuable segment of cement and concrete technology [10-15]. Due to the improved performance of concrete with IBP/SCM, WisDOT has regularly used fly ash and slag cement in pavement applications since the implementation of the Resource Conservation and Recovery Act in 1986.

For the effective use of Class F fly ash, WisDOT required further evaluation of mechanical performance. Specifically, a research need was identified to evaluate the feasibility of expanding current specifications to allow for the use of Class F fly ash in concrete paving applications. In order for Class F fly ash to be a viable alternative as a supplementary cementitious material, the resulting concrete must meet current performance standards in respect to strength (including early strength) and durability, when compared with a commonly used Class C fly ash (and other SCM).

For many years most states implemented a strategy intended to produce concrete mixtures with SCM that perform similar to concrete based on portland cement [13-15]. The specification of SCM for new pavements provides a significant contribution to sustainable development due to the application of “green” energy- and resource-saving construction materials manufactured at a lower environmental cost and with fewer greenhouse emissions. Additional savings to the WisDOT include: a) more cost-effective designs; b) more effective use of materials; c) overall longer pavement life. Savings for the traveling public and commercial vehicles include: a) fewer lane closures due to longer pavement life; b) fewer highway user delays due to the rehabilitation of lane closures for maintenance and rehabilitation activities; c) improved safety and efficiency due to fewer lane closures. Ever-increasing traffic density on Wisconsin highways makes these savings significant.

The UWM Center for By-product Utilization (CBU) is recognized for its significant contributions to effective application of fly ash in concrete. Prior work at CBU demonstrated that fly ash (40% Class F and 50% Class C) concrete can provide an excellent alternative to conventional portland cement concrete [10]. Another investigation at CBU was undertaken to examine the performance characteristics of concrete pavements made with high volumes of fly ash. Three mixture proportions with Class C fly ash were evaluated at up to 70% cement replacement and three mixtures with Class F fly ash up to 67% cement replacement were used in the study. Tests were conducted for compressive strength, resistance to chloride penetration, and density using the specimens obtained from in-situ pavements. Test results indicated a better pozzolanic strength contribution and higher resistance to chloride-ion penetration for concrete mixtures made with Class F fly ash relative to that made with Class C fly ash. Compressive strength of core specimens taken from in-situ pavements ranged between 45 to 57 MPa (6527 to 8267). The maximum compressive strength of 57 MPa (8267 psi) was achieved after 7 years, for the mixture containing 67% Class F fly ash. Field observations made in the year 2000, and continuing observations through 2002 revealed that pavement sections made with high-volumes of Class F fly ash (35 to 67%) performed well in the field, with only minor surface scaling. All other pavement sections have experienced very little surface damage due to scaling. Field performance data versus the laboratory evaluation data for scaling were reported [11].

Superplasticizing (SP, or high-range water-reducing, HRWR) admixtures have been used to increase the flow and working time of concrete mixtures over the limits achieved with conventional water-reducing (WR) admixtures [16-18]. Recent WHRP research “Laboratory Study of Optimized Concrete Pavement Mixtures” 0092-13-04 demonstrated the feasibility of application of HRWR such as polycarboxilate ether (PCE) superplasticizing admixtures in fly ash concrete. The study investigated the performance of fly ash concrete (based on fly ash Class C and F), with air-entraining admixtures and three types of water reducing admixtures at two levels of cementitious material cement contents of 280 kg/m^3 and 250 kg/m^3 (470 lb/yd^3 and 420 lb/yd^3). The early age and long-term performance parameters including the air content, fresh properties, compressive strength and durability were investigated. The results demonstrated that the use of polycarboxylate ether (PCE) superplasticizer is beneficial to boost the early strength development of fly ash concrete. However, the use of mid-range water-reducing admixture in concrete with Class F fly ash was not recommended due to significant delays of strength development (*Figure 1*).

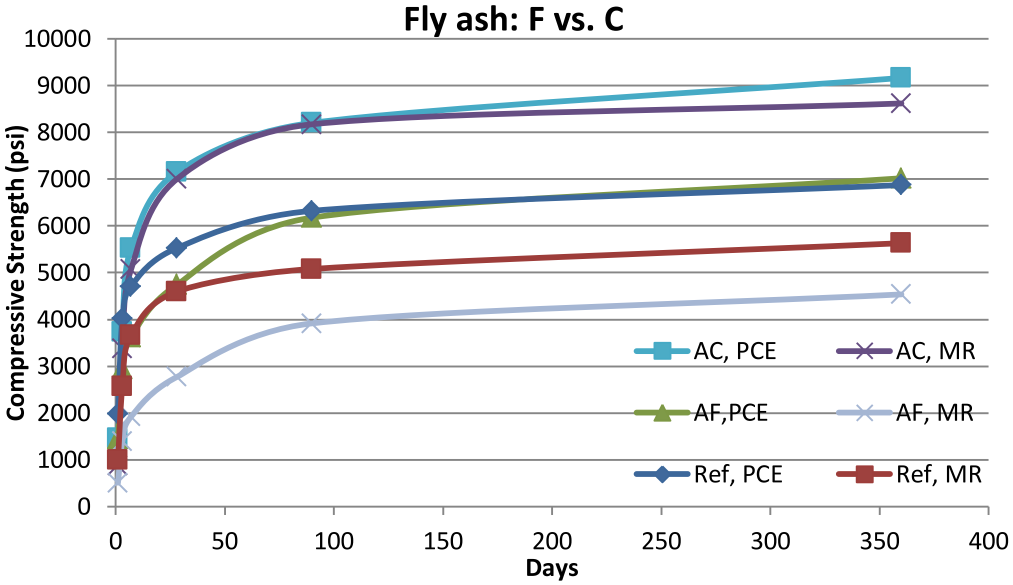


Figure 1. Compressive Strength of concrete with fly ash (WHRP 0092-13-04)

Figure 1 demonstrates that fly ash concrete with PCE admixture can achieve higher 28-day strength than the reference concrete produced with conventional water-reducing admixture (or mid-range MR). It was also demonstrated that superplasticized concrete with Class C fly ash (AC) achieves a higher early strength than the reference concrete with conventional plasticizer (MR). However, the strength of Class F fly ash (AF) concrete with "standard" MR admixture was lower than that of the reference in all ages of hardening, up to 365 days. It is a common expectation that Class F fly ash concrete has a relatively slow strength development, but, as can be observed from the reported study, even 90 days of normal curing was not sufficient to reach the strength of the reference concrete. Furthermore, the 28 day strength benchmark of 20 MPa (3,000 psi) was not achieved in concrete with Class F fly ash and MR admixture. The use of PCE admixture in place of conventional WR/MR provided a clear opportunity to design a Class F fly ash concrete capable of achieving 20 MPa (3,000 psi) in 3 days. This exceeded the strength of the reference concrete (Ref) produced with WR/MR. Therefore, it was concluded that when combined with PCE superplasticizer, Class F fly ash can be effectively used in concrete intended for paving applications.

2. MATERIALS AND METHODS

2.1. MATERIALS

2.1.1. Portland Cement

ASTM Type I portland cement from a local manufacturer was used in the reported research. The chemical composition and physical properties of cement are presented in *Table 1 and Table 2,* respectively, along with the requirements of ASTM C150 Standard Specification for Portland Cement. The chemical composition of cement was tested using X-Ray Fluorescence (XRF), Scanning Electron Microscope (SEM), and Energy Dispersive X-ray Spectroscopy (EDS) techniques. The SEM images and EDS spectra of portland cement are shown in *Figure 2* and *Figure 3*.

Table 1. Chemical composition of portland cement

Parameter	**ASTM C150 Limits**	**Test Result L2**
SiO_2	-	19.1
Al_2O_3	-	5.1
Fe_2O_3	-	2.5
CaO	-	63.3
MgO	6.0 max	2.7
SO_3	3.0 max	3.3
Na_2O	-	0.3
K_2O	-	0.6
Other	-	0.9
Ignition loss	3.0 max	2.5
Potential Composition		
Al_2O_3 / Fe_2O_3		2.1
C_4AF	-	7.5
C_3A	-	9.3
C_2S	-	4.9
C_3S	-	65.8
Na_2O_{equi}	0.6 max	0.7

Table 2. Physical properties of portland cement

Parameter	ASTM C150 Limit	Test Results L2
Specific Gravity	-	3.17
Time of setting, min		
Initial	45 min	74
Final	375 max	231
Compressive strength, MPa (psi) at the age of:		
1 day	-	17.2 (2460)
3 days	12 (1716)	28.5 (4077)
7 days	19 (2718)	32.6 (4663)
28 days	28 (4005)	40.4 (5779)

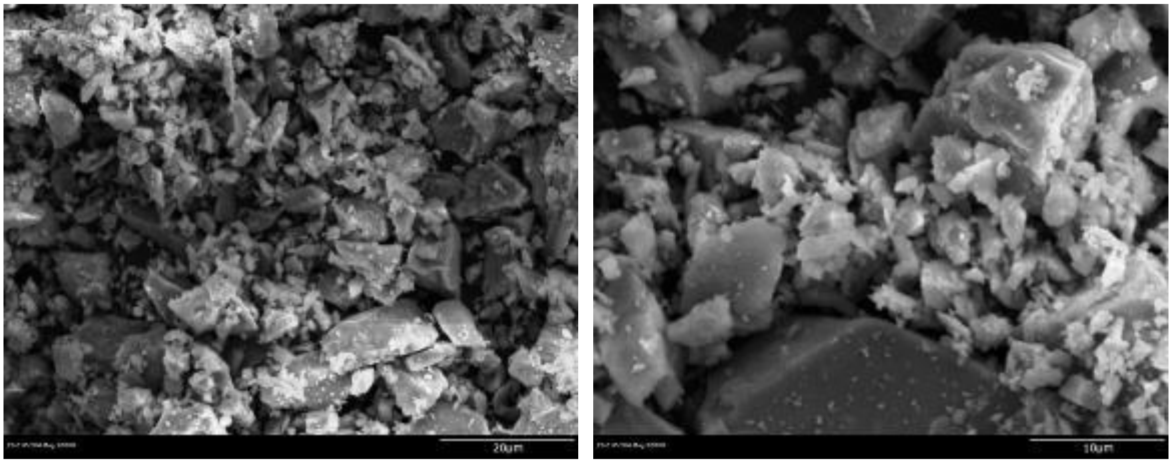


Figure 2. The SEM images of portland cement at: a) 1000x magnification, and b) 2000x magnification

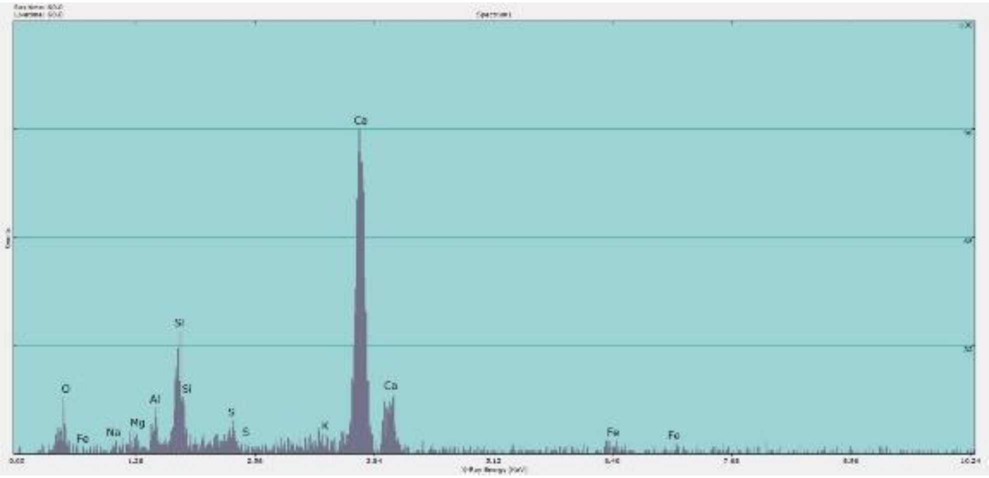


Figure 3. The EDS spectrum of portland cement

2.1.2. Fly Ash

ASTM Class C and F fly ash materials from a power station in Wisconsin were used in this research. The chemical composition and physical properties of two types of fly ash are summarized in *Table 3* and *Table 4* respectively, along with the requirements of ASTM C618, “Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete”. The SEM images and EDS spectrums of Class C and F fly ash are shown in *Figure 4* and *Figure 5*.

Table 3. Chemical composition of fly ash

Component	Chemical Composition %			
	Class F (AF)	Class C (AC)	ASTM C618 limits Class F	Class C
SiO_2	46.9	32.7	-	-
Al_2O_3	22.9	17.6	-	-
Fe_2O_3	19.2	5.9	-	-
Total, $SiO_2+Al_2O_3+Fe_2O_3$	89.0	56.2	70 min	50 min
SO_3	0.3	2.0	5.0 max	5.0 max
CaO	3.8	27.3	-	-
MgO	0.8	6.6	-	-
K_2O	1.7	0.4	-	-
Na_2O	0.6	2.2	-	-
Moisture Content,	0.1	0.8	3.0 max	3.0 max
Loss on Ignition,	2.3	0.3	6.0 max	6.0 max

Table 4. Physical properties of fly ash

Parameter	Class F (AF)	Class C (AC)	ASTM C618 limits: Class F	ASTM C618 limits: Class C
Specific Gravity	2.50	2.83	-	-
7-day Strength Activity Index, %	77.5	82.9	75 min	75 min
Water Requirement, %	102	91	105 max	105 max

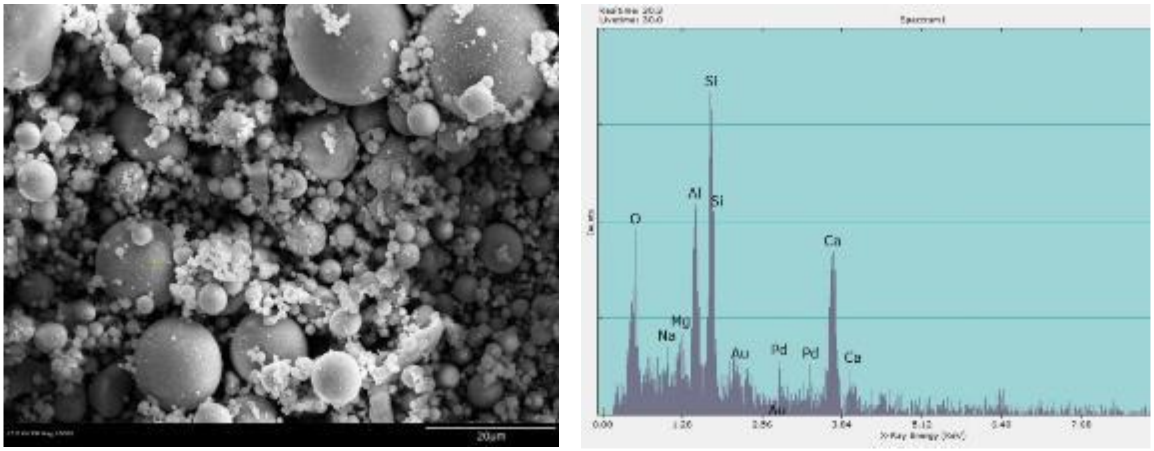


Figure 4. The SEM images and EDS spectrum of ASTM Class C fly ash

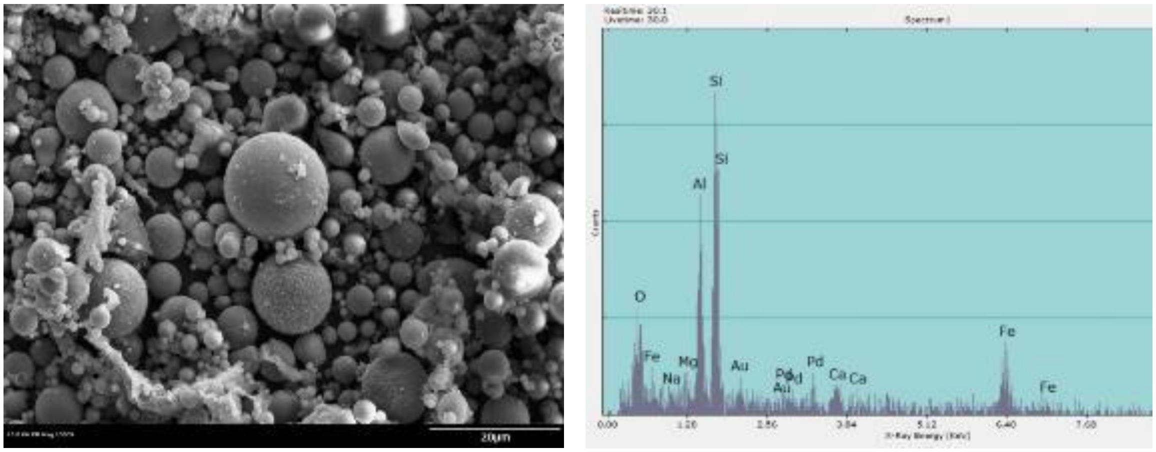


Figure 5. The SEM images and EDS spectrum of ASTM Class F fly ash

2.1.3. Chemical Admixtures

Locally available air-entraining, mid-range and high-range water-reducing (superplasticizing) admixtures were used in this study. After preliminary evaluation and screening, plasticizing (mid-range) RP8 and superplasticizing admixtures (HG7) combined with AE admixture (AMA) were selected for the research program and the properties of these admixtures are summarized by *Table 5*. The water-reducing admixtures were compared with "standard" polycarboxylate superplasticizer, Megapol 40 DF, supplied by Handy Chemicals (*Table 5*). The procedure used for the optimization of these admixtures was described by the WHRP 0092-13-04 report.

Table 5. Properties of chemical admixtures

Designation	Admixture Type	Composition	Specific gravity	Solid Content, %	Manufacturer recommended dosage *
AMA	Air-Entraining	Tall oil, fatty acids, polyethylene glycol	1.007	12.3	8-98 mL (0.13-1.5 fl oz)
RP8	Water-Reducing	4-chloro-3-methyl phenol	1.200	40.3	195-650 mL (3-10 fl oz)
HG7	High Range Water-Reducing	Polycarboxylate ether	1.062	34.0	325-520 mL (5-8 fl oz)
MP 40			1.079	38.9	65-650 mL

* *The dosage of chemical admixtures is expressed by 100 kg (100 lbs) of cementitious material*

2.1.4. Aggregates

Coarse, intermediate and fine (natural sand) aggregates supplied from Wisconsin were used in this project and *Table 6* provides a summary of aggregate types and sources. The physical characteristics of aggregates are summarized in *Table 7*. Bulk density and void content for loose and compacted aggregates are listed in *Table 8*. The sieve analysis of aggregates is provided by *Table 9* and *Figure 6*.

Table 6. Designation and sources of aggregates

Designation	Type	Location
C1	1”Limestone	Sussex Pit - Sussex, WI
I1	5/8”Limestone	Lannon Quarry - Lannon, WI
F1	Torpedo Sand	Sussex Pit - Sussex, WI

Table 7. Physical characteristics of aggregates in oven dry (OD) and saturated surface dry (SSD) conditions

Aggregate Type	Specific Gravity			Density, kg/m^3			Water Absorption, %	Fines <75μm, %
	OD	SSD	Apparent	OD	SSD	Apparent		
C1	2.730	2.765	2.829	2723	2758	2822	1.29	0.78
I1	2.684	2.734	2.824	2678	2727	2817	1.84	0.79
F1	2.566	2.637	2.762	2559	2630	2755	2.77	1.19

Table 8. Bulk density and void content of aggregates in loose and compacted state

Aggregate Type	Loose			Compacted		
	OD Bulk Density kg/m^3	SSD Bulk Density kg/m^3	Void Content, %	OD Bulk Density kg/m^3	SSD Bulk Density kg/m^3	Void Content, %
C1	1562	1582	42.7	1638	1659	39.9
I1	1466	1493	45.3	1605	1635	40.1
F1	1782	1831	30.4	1868	1920	27.0

It can be observed that the aggregate gradings were within the limits set by ASTM C33. Slight access of 300 μm fraction in sand F1 can be considered acceptable.

Table 9. Sieve analysis of aggregates (coarse, intermediate and fine aggregates)

Agg. Types	FM	Amount Finer than Sieve (mass %)									
		25 mm (1 in)	19 mm (3/4 in)	12.5mm (1/2 in)	9.5 mm (3/8 in)	4.7 mm (N. 4)	2.4 mm (N. 8)	1.2 mm (N. 16)	0.6 mm (N. 30)	0.3 mm (N. 50)	0.15 mm (N. 100)
N.67:3/4-N.4		100	90-100		40-70	0-15	0-5				
C1		100	97.4		23.4	1.1	0.2				
N.7:1/2–N.4			100	90-100	40-70	0-15	0-5	-		-	
I1			100	87.6	58.5	12.8	2.5				
Sand	2.3-3.1				100	95-100	80-100	50-85	25-60	3-50	0-10
F1	2.43				100	99	83	70	58	35	13

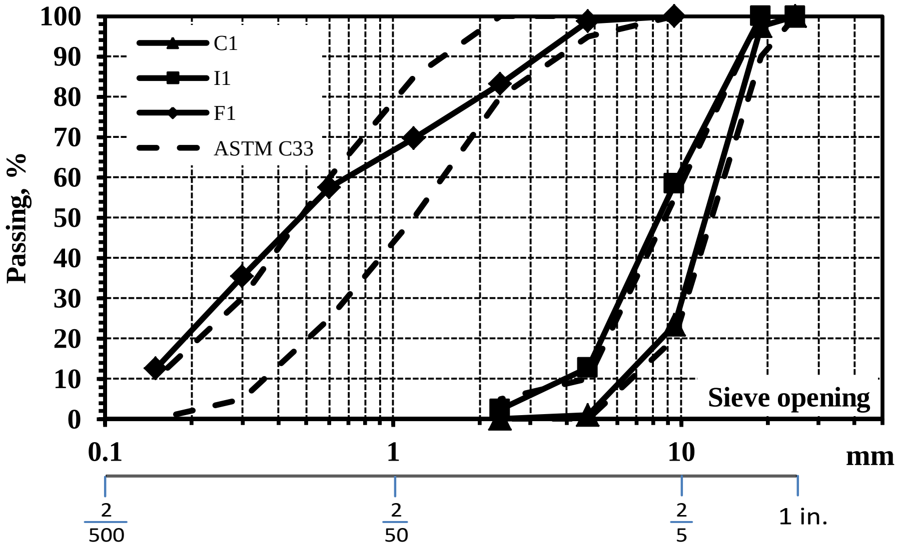


Figure 6. Particle size analysis of southern aggregates

2.2. EXPERIMENTAL PROGRAM

The experimental matrix for concrete investigation involved testing of 10 optimized mixtures containing a total of 280 kg/m^3 (470 lb/yd^3) of cementitious materials (*Table 10*). The aggregate blend was selected using 40% of coarse aggregates, 10% of intermediate aggregates and 50% of fine aggregates, which meets the optimized gradation and best packing (as per as WHRP 0092-13-04 report).

All concrete mixtures were proportioned according to the ACI 211.1 concrete specification and 211.6T technote. Concrete mixtures as per DOT specification were designed using two types of chemical admixtures (mid-range plasticizer and PCE based high-range water reducing admixture), AE admixture and fly ash. The performance of AE admixtures was evaluated in slurries as foam index with different types and proportions of fly ash corresponding to experimental composites. The reference portland cement mixtures were compared with fly ash based concrete. The resulting concrete types were evaluated for fresh properties, slump, air content, density, and temperature. The hardened properties such as the compressive strength were tested at the age of 1, 3, 7, 28 and 365 days. Durability investigation included freeze-thaw and salt-scaling tests according to relevant ASTM and AASHTO specification.

Table 10. The experimental matrix

Mix Code	**Fly Ash**		**Type of Admixture**	
	C	**F**	**Mid-Range**	**PCE**
L-M	-	-	+	-
L-H	-	-	-	+
L-M-C30	30	-	+	-
L-H-C30	30	-	-	+
L-M-F15	-	15	+	-
L-H-F15	-	15	-	+
L-M-F30	-	30	+	-
L-H-F30	-	30	-	+
L-M-C15-F15	15	15	+	-
L-H-C15-F15	15	15	-	+

Following the approach stated above, the experimental program was designed and executed. In addition, for mortars with superplasticizers, performance indicators such as compressive strength, heat of hydration (HOH), and setting time (based on HOH) were investigated. The properties of supplementary cementitious materials such as fly ash are commonly tested according to the corresponding ASTM standard, and also the results of a mortar test (ASTM C109) can be effectively used for predicting the behavior of concrete manufactured with supplementary cementitious materials (e.g., slag cement, fly ash, silica fume) and chemical admixtures [19-22]. It was proved that the strength of mortars with different quantities of SCMs is proportional to the strength of concrete based on the same binder [20]. This method can be effectively used in practice as a SCM and chemical admixtures quality control, screening and acceptance tool. The advantage of the mortar evaluation method is that it can effectively accommodate the contribution of virtually any cementitious material, mineral additive, and chemical admixture and, with sufficient accuracy, predict the performance of concrete (including strength development and the effect of admixtures).

2.3. TEST METHODS

2.3.1. Foaming Index

Foam index evaluation was performed to predict the effect of concrete mixture components, especially fly ash on the stability of the air void system and the dosage of air-entraining admixture (AEA) required to achieve a specific air volume in fresh concrete. Generally, the dosage of AEA depends on the type and chemical structure of this component, other incorporated admixture, as well as the composition of cement and cementitious materials.

The test procedure used the method developed by Hover et al. [23] and was modified to use the mechanical agitation and also additional time periods to estimate the stability of foam. The experiment involved six compositions with varying cement and fly ash proportions, as presented in *Table 11*. A water solution of AEA (10% diluted) was used for the test.

Table 11. Mixture proportions of investigated cement and fly ash compositions

Sample ID	Composition, %			W/CM
	Cement	Fly Ash		
		Class C	Class F	
R	100	-	-	2.5
C15	85	15	-	2.5
F15	85	-	15	2.5
C30	70	30	-	2.5
F30	70	-	30	2.5
CF	70	15	15	2.5

The test procedure involved mixing of cement and fly ash (if any) with tap water. The jar with the blend was sealed and subjected to mechanical agitation for 1 minute using an adapted shaker (from ELE Instruments). The AEA water solution was added to the mix 1-2 drops at a time. The weight of each drop was 50 mg (0.0001 lb) or 50 ml (0.002 fl.oz). After each addition, the jar was sealed and exposed to agitation for 15 seconds, and then the stability of the foam was observed. Foam was considered to be stable, when the bubbles uniformly covered the entire surface of the tested suspension with the same height for at least 45 seconds. If foam was not stable after the first addition of the AEA, the same procedure (the addition of AEA and agitation for 15 seconds) was repeated until the stable foam was observed. The same testing procedure was used for all six compositions in order to calculate the foam index. The foam stability was initially tested at 45 seconds and monitored after 1, 5, 20, 40 and 60 minutes of agitation.

Using the recorded dosage of AEA, the volume of droplets as well as the quantity of the solid components (fly ash and cement) the parameters of Foam Index, Absolute Volume, Specific Foam Index, Relative Foam Index and Stability were calculated using the following equations:

$$\textbf{Foam Index} = \textbf{ND} * \textbf{0.05}\ [\text{mL}] \tag{1}$$

where ND is the number of AEA solution drops added; 0.05 is the volume of AEA solution per drop, ml (this value may vary depending on the apparatus used to produce a drop).

$$\textbf{Absolute Volume = Foam Index * CS} \quad \text{[ml AEA]} \tag{2}$$

where CS is the concentration of AEA, g/liter.

$$\textbf{Specific Foam Index = Absolute Volume * 10,000} \text{ [ml AEA/100 kg CM]} \tag{3}$$

$$\textbf{Relative Foam Index = [(Abs. Vol. Ash Mix)/ (Abs. Vol. Cement)] * 100} \text{ [\%]} \tag{4}$$

$$\textbf{Stability} = \mathbf{H_{60}/H_0*100} \text{ [\%]} \tag{5}$$

where H_{60} is the height of foam after 60 minutes at rest; H_0 is the initial height of foam.

2.3.2. Mortar Tests

For mortar specimens, the water to cementitious material (W/CM) ratio of 0.45 and 0.4 was selected, for mixtures with WR and HRWR, respectively, and the sand to cement (S/CM) ratio was set to 1. The W/CM ratio was reduced from that specified by the ASTM Standard (W/C=0.485, ASTM C109) due to the use of water-reducing admixtures. Also, the W/C was selected to provide a reasonable workability for tested compositions and to enable comparison of the effects of chemical admixtures at different dosages without poor compaction or segregation. These parameters were close to the mortar phase used in the investigated concrete. The mixing of mortars was performed as specified by ASTM C109 and ASTM C305. The workability and density of fresh mortars was evaluated as specified by ASTM C 1437 and ASTM C 138, respectively.

For the compressive strength investigation, cube mortar specimens with the dimensions of 50 × 50 × 50 mm (2 × 2 × 2 in.) were cast and cured in accordance with ASTM C 109. Test samples were removed from the molds after 24 hours of curing, immersed in a lime water, cured at a temperature of 23±2Cº, and then tested at the age of 1, 7 and 28 days. The compressive strength of the mortar specimens was determined using a pace rate of 1.4 kN/s (315 lb/s). The reported values represent a mean of at least two specimens tested for each age.

2.3.3. Heat of Hydration

An isothermal calorimeter measures the rate of heat release from the hydrating mixtures due to ongoing chemical reactions. In this study, an isothermal calorimeter TAM Air (from TA Instruments) was used to evaluate the hydration kinetics at a constant temperature of 25 °C during the early 48-hour period. The output of the calorimeter was evaluated by graphical and mathematical means to evaluate the effect of different combinations of components. The isothermal curves or hydration profiles were used to indicate the setting characteristics, compatibility of different materials, early strength development, and the effect of chemical admixtures.

2.3.4. Preparation, Mixing, and Curing of Concrete

Concrete batching, mixing, casting and curing procedures were conducted according to ASTM C192 "Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory". The mixing procedure included mixing of aggregates with 20% of total water for 30 seconds using a drum mixer suitable for the volume of the batch. Next, cement was added to the mix, and then fly ash (when required) was added. The rest of the water with chemical admixtures was added upon the addition of cementitious materials. Finally, sand was added to the mixer. The mixing was resumed for an additional 3 minutes. The mix was left in the drum mixer at rest for a period of 3 minutes and was then mixed for another 2 minutes. The total mixing was approximately 10 minutes.

2.3.5. Fresh Properties

A concrete slump test was performed according to ASTM C143 to measure the workability of fresh concrete. This test is widely used in the field to determine the suitability of concrete pavement mixtures for slip-forming; however, there are other characteristics such as finishability that are not characterized by this test. In order to evaluate the slump loss, the test was repeated at a time corresponding to 30 minutes of hydration (from the initial contact of water and cement).

The density of fresh concrete was tested per ASTM C34. All the mixtures, regardless of the slump, were consolidated using rodding and tapping the side of the container with a rubber mallet repeated for 3 layers. The top of the container was leveled off and the weight was measured using a scale per ASTM C34.

Concrete air content was tested in the fresh state using the pressure method with an air meter as per as ASTM C231. Optimized concrete mixtures were designed to reach air content of 6±1.5%; however, some fluctuations occurred due to the variation in type of admixtures and fly ash.

Fresh concrete temperature was tested according to ASTM C164 to monitor the potential effect of temperature. The temperature can be used to track any potential variation in different batches due to moisture loss, as well as heat of hydration.

2.3.6. Compressive Strength

Compressive strength tests were performed on concrete cylinders with a diameter of 102 mm (4-in.) and height of 203 mm (8-in.) according to ASTM C39. These specimens were tested with an ADR-Auto ELE compression machine at a loading rate of 2.4 kN/s (540 lb/s). The maximum load and maximum compressive stress were recorded. The test was performed at different ages including 1, 3, 7, 28, 90 and 365 days of normal curing.

2.3.7. Resistance to Rapid Freezing and Thawing

From each batch of concrete, two 76 x 102 x 406 mm (3 x 4 x 16 in.) beams were produced. The specimens were moist-cured for 28 days and then conditioned in a lab environment at a relative humidity of 50% and a temperature of 70 °F. The testing for freeze-thaw durability followed the procedure of the Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing (ASTM C 666, equivalent to AASHTO T161), Procedure A and Standard Test Method for Fundamental Transverse, Longitudinal, and Torsional Resonant Frequencies of Concrete Specimens ASTM C 215 with an exception related to the conditioning prior to testing.

At the age of 56 days, each specimen was saturated in water for 48 hours. The purpose of this saturation process was to make the initial measurements comparable to later conditions of the specimen. This follows the instructions for conditioning beams cut from the hardened concrete stated in the provision 8.1 of ASTM C666. Immediately after the conditioning period (at the age of 56 days), the fundamental traverse frequency of the specimens was measured according to the ASTM C215. Mass, average length and cross-section dimensions were measured within the tolerances required by Test Method C215.

Freezing and thawing tests were started by placing the specimens into containers with water at the beginning of the thawing phase of the cycle. Each cycle included freezing for 2-hour exposure at -18°C (0°F) and thawing for 2-hour exposure at 10°C (50°F). The freezing and thawing test was programmed and conducted using an environmental chamber. The specimens were removed from the apparatus at 50 freezing cycles' intervals and tested for the fundamental traverse frequency and mass change. The specimens were then returned to the apparatus and further subjected to freeze-thaw cycling. Each specimen was tested for a total of 300 cycles or until the relative dynamic modulus of elasticity reached 60 % of the initial modulus. The relative dynamic modulus of elasticity of was calculated as follows:

$$\mathbf{P_C = (n_C/n_O)^2 \times 100} \quad [\%]$$

where n_O and n_C are the fundamental transverse frequency, before and after freezing and thawing test, respectively.

The durability factor of each specimen was calculated as follows:

$$\mathbf{DF = PN/M}$$

where P is the relative dynamic modulus of elasticity at N cycles, %; N is the number of cycles at which P reaches the specified minimum value for discontinuing the test or the specified number of cycles at which the exposure is to be terminated, whichever is less; and M is the specified number of cycles.

2.3.8. Salt-Scaling Resistance

The salt-scaling resistance test was conducted according to ASTM C 672. The ASTM C 672 defines the test procedure for the resistance to scaling of a horizontal concrete surface exposed to freezing and thawing cycles in the presence of deicing chemicals. The evaluation of surface resistance is conducted qualitatively by visual examination and also quantitatively by calculating the mass loss due to the salt scaling. The experimental procedure used 254 x 254 x 66 mm (10 x 10 x 2.6 in.) duplicate specimens.

For all concrete types, the specimens were removed from the moist storage at the age of 28 days and conditioned in air for 14 days at 23 ± 2°C (73.5 ± 3.5° F) and at 45 to 55 % relative humidity.

After completion of curing and conditioning the top surface of specimens was immersed into a container with at least of 6 mm (1/4 in.) of a solution of calcium chloride and water covering the specimens (at a concentration such that each 100 mL of solution contains 4 g of anhydrous calcium chloride as per ASTM C672). The specimens were placed in a freezing environment for 24 hours. Upon the completion of this period, the specimens were removed from the freezer and thawed in a laboratory at 23 ± 2 °C (73.5 ± 3.5 °F) for 24 hours. The surface was flushed off thoroughly at the end of each 5 cycles and subjected to visual examination. At this stage the solution was replaced.

The samples were subjected up to 50 cycles of freezing and thawing, according to the Standard ASTM C 672, and a visual inspection of the exposed side of the surface was also performed. The surface scaling due to freezing and thawing in the presence of deicing chemicals was rated between zero to five, zero being the highest resistance ("no scaling") and 5 being the lowest resistance ("severe scaling") to salt.

3. RESEARCH RESULTS AND DISCUSSION

3.1. EVALUATION OF CHEMICAL ADMIXTURES

3.1.1. Foaming Index

In this study, to estimate the efficiency of AEA in fly ash, the foam index test was performed. All the calculated parameters are reported in *Table 12.*

Table 12. The Foam Index characteristics related to the application of AEA

Mix ID	**Foam Index, ml**	**Absolute Volume, ml AEA**	**Specific Foam Index ml/100 kg CM**	**Relative Foam Index, %**	**Average Height of Foam, mm (in)**		**Stability, %**
					Initial	**After 60 minutes**	
R	0.41	0.04	416	100	6 (0.24)	6 (0.24)	100
C15	0.57	0.06	572	138	8 (0.31)	5.8 (0.23)	73
F15	0.52	0.05	520	125	6.5 (0.25)	5.5 (0.22)	85
C30	0.68	0.07	676	175	7.3 (0.29)	6.3 (0.25)	86
F30	0.88	0.09	884	213	7.5 (0.3)	5.0 (0.20)	67
CF	0.57	0.06	572	138	6.8 (0.27)	5.1 (0.20)	75

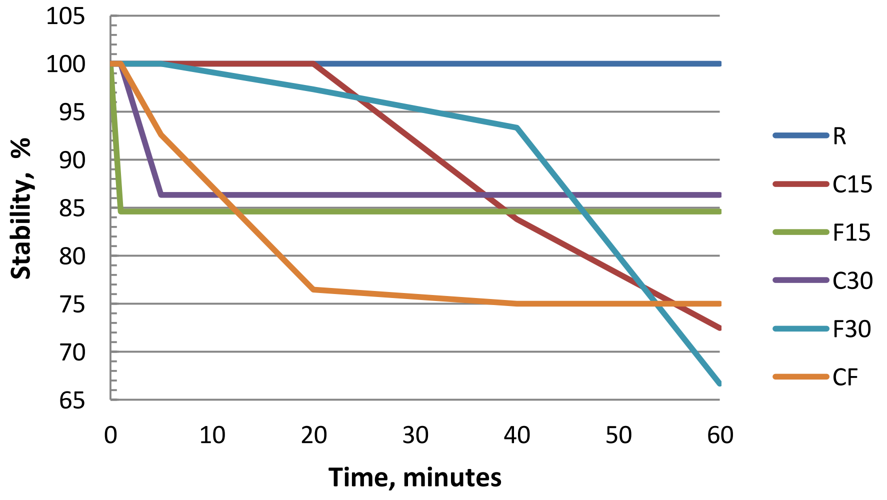
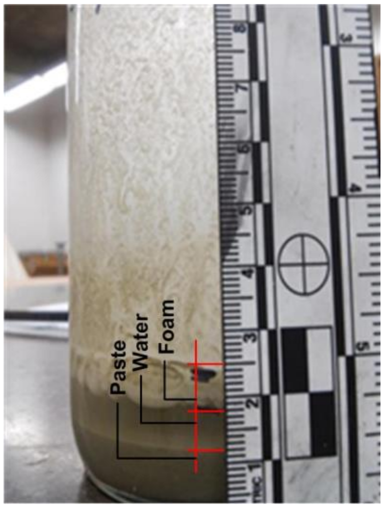


Figure 7. The Stability of foam for cement-fly ash compositions



C15 (foam height ~8 mm)

Figure 8. Stability of foam structure of cement-fly ash compositions

The calculated Foam Index values for all six compositions prove that the addition of up to 30 % fly ash requires more AEA to achieve stabile foam. Still, the compositions with 15% of fly ash (C15 and F15) as well as the combination of Class F and C fly ash (CF) with a total percentage of 30% demonstrated a similar demand of AEA, up to 40% higher than the reference portland cement. At the same time, the reference portland cement composition had the minimal demand of AEA to achieve the foam stability for the period of up to 60 minutes.

Observing the foam stability over time, different behavior was detected for the compositions. For the reference composition, the height of the foam was recorded to be the same over 60 minutes, but the foam started breaking in the center of the jar after 5 minutes after agitation, so only about 93% of the surface of the suspension was covered by the foam at the end of the experiment. Due to a relatively low dosage of AEA, the reference mix had the lowest initial foam height among all the other compositions containing fly ash. The composition C15 had 27% reduction of the foam height after 60 minutes.

The composition F15 demonstrated about 16% drop in height after 5 minutes, but kept stable foam with uniform covering on the suspension surface for all 60 minutes of observation. Similar behavior was demonstrated by the C30 mix with 14% reduction in foam height detected after 5 minutes of agitation. At this point, the foam was stabilized and did not change for the rest of the observations. However, the foam structure was weak and easily broken under slight shaking. The suspension, containing up to 30% of fly ash Class F demonstrated the highest 34% reduction in foam height. After 5 minutes of mixing and agitation, the foam height started to drop. However, for the rest of the observations, the foam bubbles covered the suspension surface uniformly without any visible changes. However, the foam was weak and easily collapsed upon slight shaking. The suspension of the 15% + 15% combination of fly ash Class C and F also had a significant 25% reduction in foam height during the experiment. The foam height started to drop after 1 minute and kept dropping over 20 minutes. After that point, the foam was stabilized with no visible distortion observed until the end of the experiment.

The use of fly ash (Class F and C) in the portland cement systems increase the AEA demand, and the addition of 30% Class F fly ash results in the highest dosage of AEA. At a small percentage of fly ash, the stability of the foam was better. Tests with WR/HRWR are recommended as these admixtures can compromise the stability of the foam.

3.1.2. Heat of Hydration

The performance of fly ash based mortars with plasticizing (RP8) and superplasticizing (HR1/ HG7) admixtures was investigated and compared to a reference mortar using the parameters of the hydration process detected by the isothermal calorimeter. For this study, mortars based on portland cement (L2) were monitored for the early hydration period of 48 hours. The observed effects are represented by *Figure 9* and *Figure 10* reporting on the performance of mortars with RP8 and HG7 admixtures, respectively.

It can be observed that mortars with all types and combinations of fly ash are characterized by the delay of the hydration and lower rate of hydration compared with the reference. The blended cement system with Class C and Class F fly ash blend and MR admixture demonstrated a slight (about 2 hours) extension of the dormant period and the reduction of the intensity of the C_3S peak. In addition, the 2nd peak (corresponding to

C_3A) appeared with a delay of 5 hours. Such delays can be beneficial for summer applications, reducing the slump loss and preserving workability while in transit to the jobsite. With the addition of Class F fly ash, the intensity of the main exothermal peak was reduced, possibly because of the selective action of the admixtures, delaying the hydration of C_3A by about 2 hours.

The addition of PCE superplasticizer resulted in some acceleration of cement hydration vs. observed for mid-range plasticizing admixture with the main peak of higher intensity appearing around 3 hours earlier (vs. corresponding peak of mortars with MR).

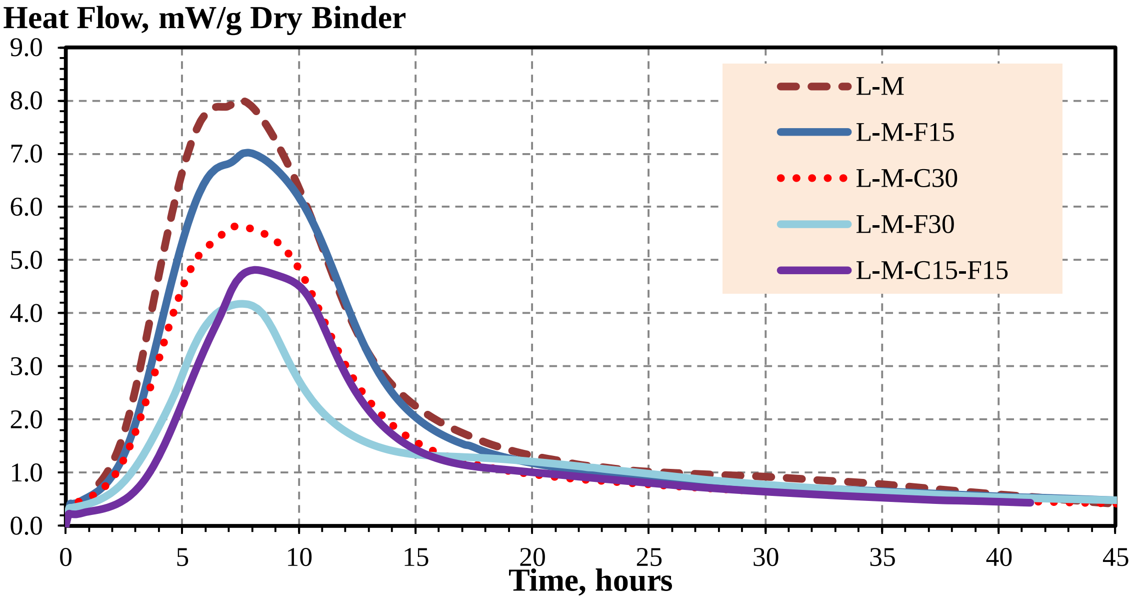


Figure 9. The hydration of blended cement compositions with the Class C and F fly ash mid-range water reducing admixture.

The use of PCE superplasticizer (HG7) in blended cement mortars with Class C fly ash results in the reduction in the heat flow and a delay (shift) of the peak. More significant delay occurs for mortars with 30% of Class F fly ash. Here, the use of Class F fly ash results in a considerable decrease of the heat response associated with C_3S and to a lesser extent C_3A. However, superplasticized mortars with 15% of Class F fly ash had very little reduction of the peak heat flow, suggesting excellent mechanical performance. These observations are commonly verified and supported by strength testing.

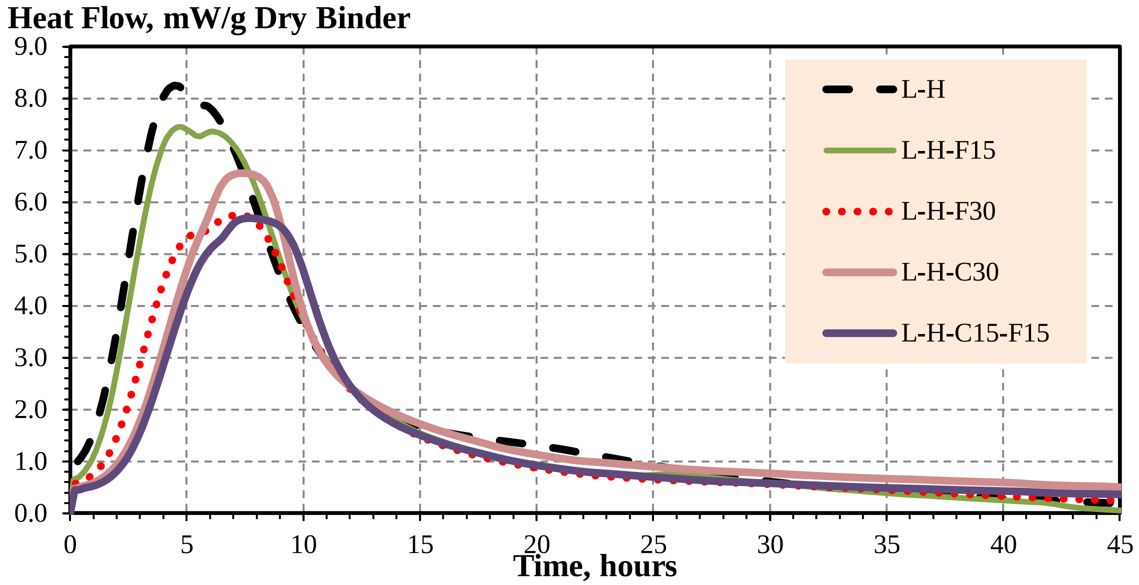


Figure 10. The effect of PCE admixture on cement hydration of blended cement systems with fly ash.

3.1.3. Setting time

Portland cement hydration is an exothermal reaction affected by the addition of chemical admixtures and supplementary cementitious materials. The isothermal conduction calorimeter (TAM Air from TA Instruments) was used to monitor the hydration process for 72 hours at 21±1 C°. The output of the calorimeter was used to evaluate the performance related to setting and early strength development. The initial setting time (IST) was calculated when the slope of the isothermal curve increased from zero to a positive value. The final setting time (FST) was calculated as the time required to reach 50% of the average maximum power corresponding to the main hydration peak as described in [24].

The extension of an initial setting time was due to the addition of Class C and F fly ash as reported in *Table 13*. It is evident that the replacement cement with supplementary cementitious material results in delayed setting times.

Table 13. Setting time of investigated compositions (based on HOH test)

ID	Setting Time			
	Initial		Final	
	hours	minutes	hours	minutes
L-M	1.4	84	3.8	228
L-M-F15	1.6	96	3.7	222
L-M-C30	1.2	72	4.1	246
L-M-F30	1.4	84	3.9	234
L-M-C15-F15	2.0	120	4.9	294
L-H	0.2	12	2.1	126
L-H-F15	0.4	24	2.4	144
L-H-F30	0.8	48	2.9	171
L-H-C30	1.2	72	3.9	231
L-H-C15-F15	1.0	60	3.5	210

3.2. MORTARS: THE EFFECT OF FLY ASH

3.2.1. Fresh Properties

Tests for flow and fresh density of mortars were used to evaluate the effect of fly ash and its compatibility with chemical admixtures. The performance of mortars with fly ash was compared with the properties of a reference mortar (Ref L). Relevant ASTM standards were used for the evaluation of mortar flow (ASTM C 1437) and fresh density (ASTM C 138). The research results are reported in *Table 14*. Such mortar tests can be effectively used to evaluate the content of fly ash and compare to reference SCM (such as metakaolin) and verify the interaction with chemical admixtures. Using these tests, the dosage of plasticizing admixtures and superplasticizers was verified based on the flow response and density performance.

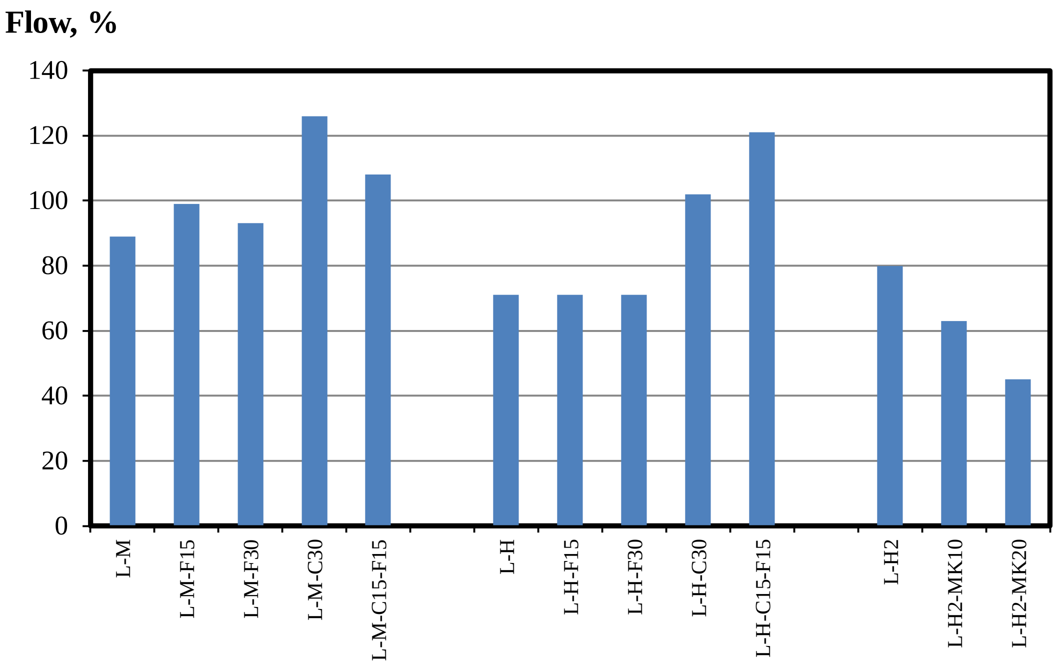


Figure 11. The effect of chemical admixtures on mortar flow

Portland cement mortars with reference SCM such as metakaolin at up to 20% dosage and reference PCE (MD40) demonstrated a considerable reduction in flow (*Table 14*).

In the systems with fly ash, the relative flow enhancement was more significant when mid-range plasticizers were used in combination with Class C fly ash. This can be explained by different absorption capacities of cements and fly ash; therefore, cement replacement with fly ash, absorbing lower quantities of surfactants is equal to a relative increase in the admixture dosage. Therefore, in the systems with Class C fly ash, the dosage of chemical admixtures can be reduced to avoid the overdose and potential delay in strength development (especially in the case of plasticizer). In the case of synergy between the superplasticizer and fly ash, improved workability can be used to boost the strength of concrete (by reducing W/CM ratio) or to reduce the cementitious material content (at a constant W/CM ratio).

3.2.2. Mechanical Performance

The effect of fly ash types and combinations with chemical admixtures was evaluated by testing the compressive strength of mortars at different stages of hardening. The performance of investigated compositions is summarized in *Table 14* and further demonstrated by *Figure 12* and *Figure 13*.

Table 14. The effect of fly ash and metakaolin on the performance of mortars

Mortar Mix ID	Flow, %	Compressive Strength, MPa (psi) at the Age of		
		1 days	7 days	28 days
L-M	89	7.5 (1088)	23.5(3408)	31.1(4510)
L-M-F15	99	9.3(1349)	21.4(3103)	31.6(4582)
L-M-F30	93	6.9(1001)	18.4(2668)	31.1(4510)
L-M-C30	126	7.1(1030)	15.9(2306)	27.8(4031)
L-M-C15-F15	108	15.7(2277)	22.0(3190)	30.7(4452)
L-H	71	21.8(3161)	40.8(5916)	45.9(6656)
L-H-F15	71	20.7(3002)	34.3(4974)	41.6(6032)
L-H-F30	71	14.5(2103)	27.3(3959)	38.1(5525)
L-H-C30	102	9.7(1407)	27.8(4031)	39.4(5713)
L-H-C15-F15	121	8.6(1247)	25.2(3654)	31.8(4611)
L-H2	80	25.2(3654)	41.6(6032)	53.5(7758)
L-H2-MK10	63	20.6(2987)	43.6(6322)	56.6(8207)
L-H2-MK20	45	19.1(2770)	42.9(6221)	59.3(8599)

It can be observed that the use of plasticizing admixture RP8 vs. superplasticizer results in a reduction of strength at all hardening ages. Surprisingly, the 1-day strength of mortars with the combination of Class C and F fly ash was over performing the strength of the reference L-M and had a very comparable strength at 7- and 28- day age, as reported by *Figure 12*. The compressive strength of all mortars modified with mid-range water reducing admixture was considerably lower than that observed for corresponding mortars with PCE superplasticizer (with the exception for 1-day strength of mortars with Class C fly ash and 15+15 fly ash blend). This is due to lower W/CM ratio used in the systems with superplasticizer. This is a clear sign that the use of PCE admixture is very beneficial in portland cement and blended cement with SCM (up to 50% improvement).

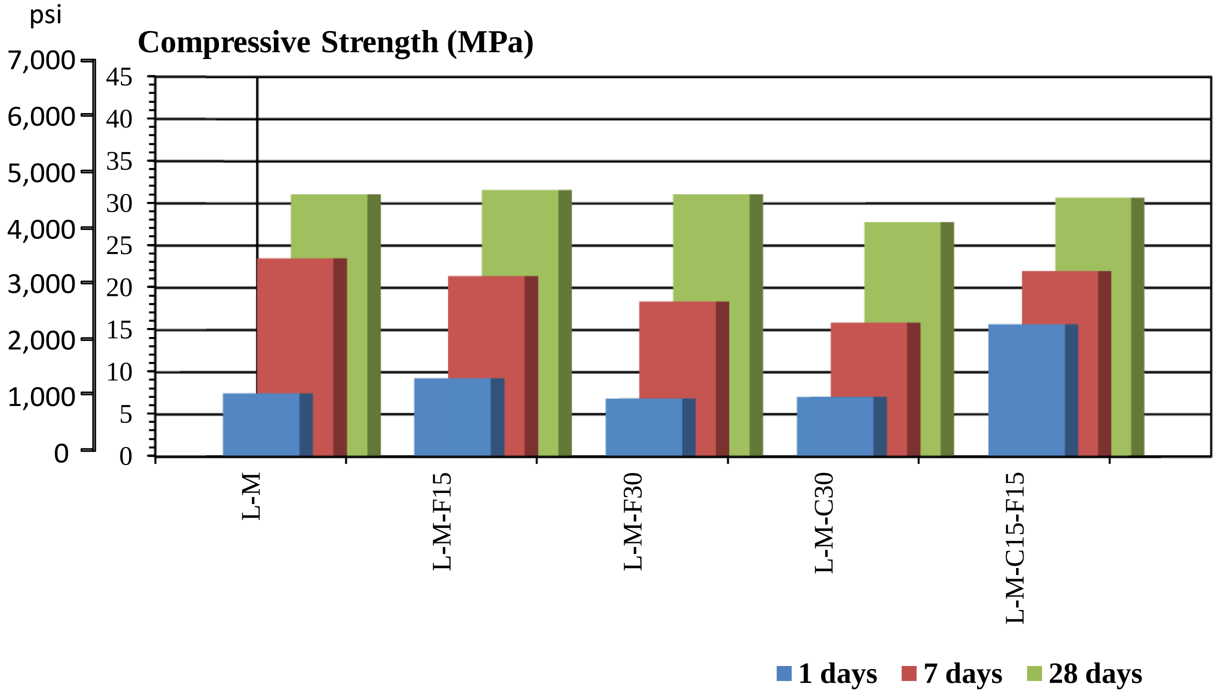


Figure 12. Compressive strength of mortars with mid-range water-reducer (RP8)

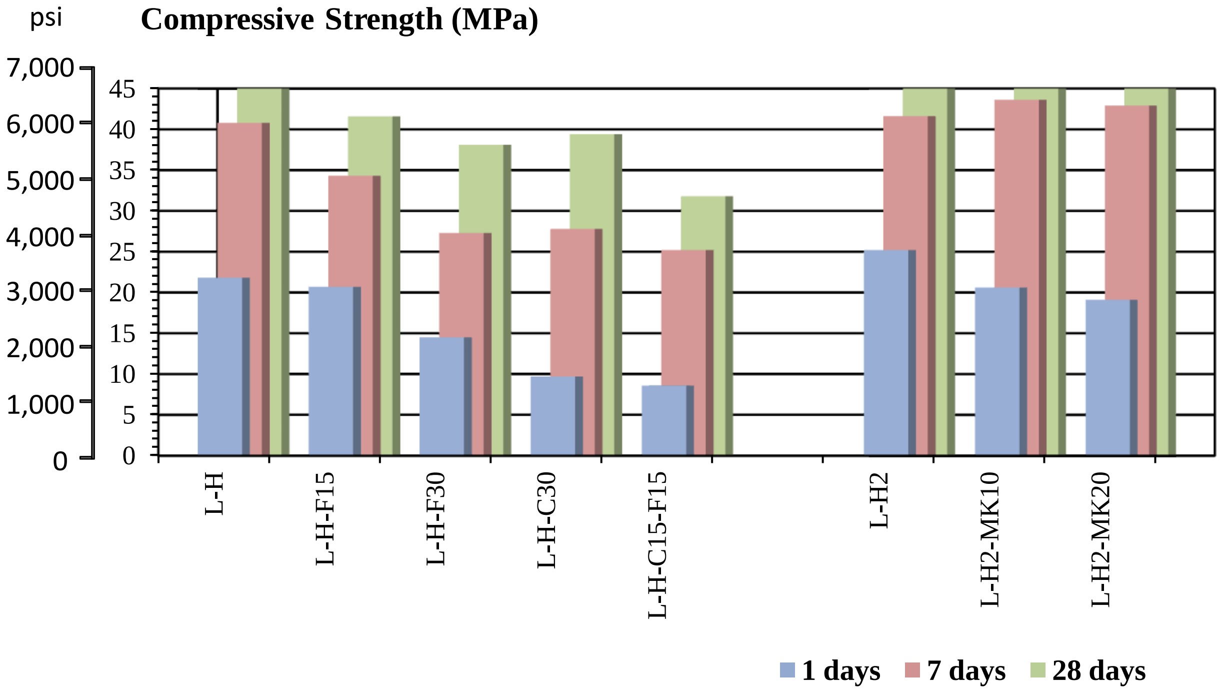


Figure 13. Compressive strength of mortars with PCE superplasticizer (HG7 and MD40)

The use of reference superplasticizer (MD40) and also reference SCM product metakaolin demonstrated the potential to further boost performance (*Table 14*). This option can be explored in the future.

3.3. PROPERTIES OF CONCRETE MIXTURES

This study reports on the performance of optimized eco-friendly fly ash concrete designed with 280 kg/m^3 (470 lb/yd^3) of cementitious materials.

These concrete mixtures were produced with fly ash, mid-range plasticizer or high-range water reducer, and AE admixture. Fresh properties such as slump, air content, and fresh density were analyzed. Furthermore, the compressive strength was investigated at different ages of hardening. The durability investigation involved tests on freeze-thaw and salt-scaling resistance.

3.3.1. Target Properties

The mixture proportions of concrete with 280 kg/m^3 (470 lb/yd^3) are reported in *Table 15*. The fresh and hardened properties of concrete are presented in *Table 16*. The lowest desirable W/CM ratio that results in a slump of 50-100 mm (2-4 in.) was selected for different compositions with mid-range water reducing and superplasticizing admixtures. Other target parameters were air content of 7±1.5% and early (7-day) compressive strength of 20 MPa (3,000 psi).

3.3.2. Fresh Properties

Workability of concrete mixtures was evaluated using the slump test. Concrete slump depends on various parameters, including W/CM ratio, water and cement content (the volume of cement paste), aggregate packing and gradation, the type of chemical admixtures, and the volume of air controlled by the dosage of AE admixtures. The optimal dosage of mid-range water reducing and superplasticizing admixtures (RP8, HG7, respectively) was established by the WHRP 0092-13-04 report at the level of 0.15%. In this study, the proportioning of aggregates was held constant for each composition; therefore, the effect of this parameter on the slump was eliminated. The workability of fresh concrete was evaluated right after the mixing and also at one hour after the initial contact of cement with water (in the mixer) and is reported in *Table 16*. The reference concrete with mid-range plasticizer (RP8) produced at W/CM ratio of 0.45 (L-M) had a lower workability than concrete with PCE superplasticizer (HG7) produced at a reduced W/CM of 0.4.

Concrete with mid-range plasticizers (L-M-C30, L-M-F30) and fly ash (Class C and Class F) produced at the same W/CM ratio of 0.45 had a similar slump within the range of 10-60 mm (0.4-2.4 in.) as corresponding concrete with superplasticizer at W/C ratio of 0.4, which was characterized by the slump of 5- 64 mm (0.2-2.5 in.). When using Class F fly ash though, concrete mixtures may require the use of higher water content to achieve the same levels of workability as attained by Class C fly ash concrete mixtures. This correlates with the increased water demand of Class F fly ash mortars. In spite of relatively low slump values, all investigated mixtures had excellent workability and were easily compacted and finished with hand tools. The air content of all fly ash based concrete was within the limits of 4.7–8%. The air content of mixtures can be correlated with fresh density as illustrated in *Figure 14*. Although the air content for concrete with less than 6% are scattered, the mixtures with air content that is greater than 6% have a strong linear relationship with fresh density. To extend the freeze-thaw performance of concrete, the dosage of AE admixture may need to be further increased to ensure the required air volume, air void structure and spacing factor (*Figure 14*).

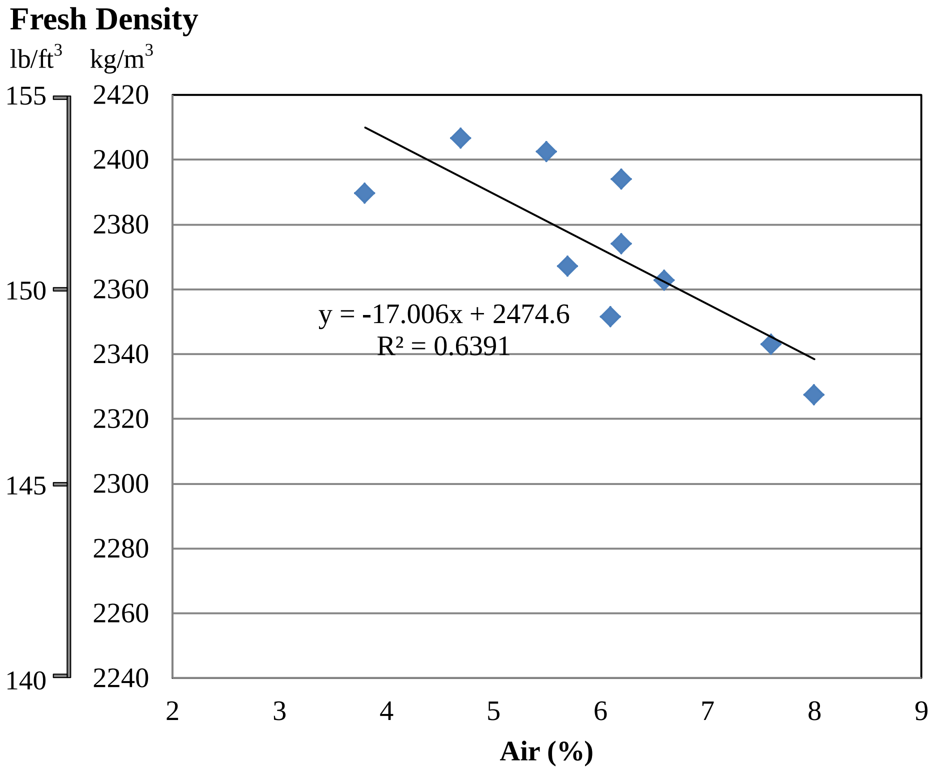


Figure 14. The relationship between the air content and fresh density of concrete mixtures

3.3.3. Strength Development

Superplasticizing admixtures were effectively used to achieve the required air content and slump parameters at the lowest W/CM ratio with the goal of obtaining improved mechanical performance. Here, a higher compressive strength can be achieved at a lower W/CM ratio; however, using a lower W/CM ratio may result in impractical workability levels and poor compaction. Using an effective superplasticizer such as PCE can provide the reduction of W/CM and excellent workability. The mechanical performance of investigated concrete was evaluated for early (1-7 days) and long-term (28 days) periods and up to 365-day periods.

As demonstrated by *Figure 15* below, the highest compressive strength was achieved by concrete with 30% of Class C fly ash and PCE superplasticizer; this concrete had the 7-day strength of 33 MPa (4,787 psi) and 28-day strength of 43.8 MPa (6,380 psi). The 365-day strength of this concrete was at the level of 47.3 MPa (6,860 psi). This proves that the use of PCE admixtures in concrete with Class C fly ash can provide superior performance in terms of workability and strength development.

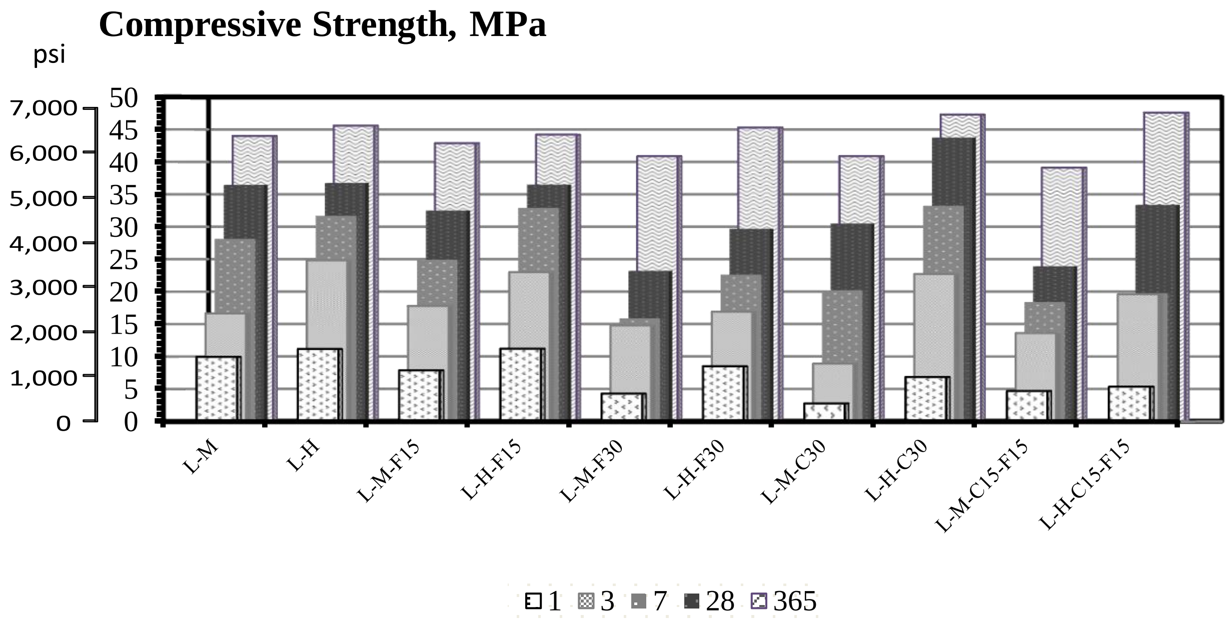


Figure 15. The effect of fly ash on strength development of concrete

Concrete with 15% of Class F fly ash had demonstrated strength development similar to that of reference concrete with corresponding chemical admixture.

At the age of 7-days, almost all concrete types exceeded the standard level of 20 MPa (2,900 psi), except for the concrete mixtures with mid-range plasticizer containing 30% of Class F fly ash or 15%+15% fly ash blend. This is due to the combined retardation effect of Class F fly ash and mid-range plasticizer. In almost all the cases and, especially, at early ages of hardening, the strength of concrete with PCE superplasticizer was higher than that of concrete with mid-range plasticizer, possibly because of using lower W/CM of 0.4 (vs. 0.45). However, this difference was less pronounced at the age of 28 days and later. The strength of concrete based on 15%+15% blend of Class F and C fly ash modified with superplasticizer was at an acceptable level, reaching the best 365-day compressive strength of 47.7 MPa (6,918 psi).

Table 15. Mixture proportions used for concrete with cementitious material content of 280 kg/m^3(470 lb/yd^3)

a) SI Units

Cement Factor	**Mix ID**	**Dosage of Admixtures, %**			**Mixture Proportions, kg/m^3**									
					Cement	**SCM**		**Aggregate (SSD)**				**Admixtures**		**Total Water**
		PCE	Mid-Range	AE		FAF	FAC	CA	IA	FA	Total	WR HRWHA	Air Entraining	
280 kg/m^3 (470 lb/yd^3)	L-M		0.150	0.010	280	0	0	793	195	932	1920	0.620	0.199	158
	L-H	0.150		0.010	280	0	0	793	195	932	1920	0.812	0.199	157
	L-M-F15		0.150	0.010	238	42	0	789	194	928	1911	0.620	0.199	157
	L-H-F15	0.150		0.010	238	42	0	804	198	945	1947	0.812	0.199	144
	L-M-F30		0.150	0.015	196	84	0	785	193	922	1900	0.620	0.298	158
	L-H-F30	0.150		0.015	196	84	0	800	197	940	1937	0.812	0.298	144
	L-M-C30		0.150	0.005	238	0	42	790	194	928	1912	0.620	0.099	158
	L-H-C30	0.150		0.010	196	0	84	805	198	946	1949	0.812	0.199	144
	L-M-C15-F15		0.150	0.010	196	42	42	787	193	925	1906	0.620	0.199	158
	L-H-C15-F15	0.150		0.010	196	42	42	802	197	943	1942	0.812	0.199	144

b) US Customary Units

Cement Factor	Mix ID	Dosage of Admixtures, %			Mixture Proportions, lb/yd^3									
					Cement	**SCM**		**Aggregate (SSD)**				**Admixtures**		**Total Water**
		PCE	Mid-Range	AE		FAF	FAC	CA	IA	FA	Total	WR HRWHA	Air Entraining	
280 kg/m^3 (470 lb/yd^3)	L-M		0.150	0.010	472	0	0	1337	329	1571	3236	1.045	0.335	266
	L-H	0.150		0.010	472	0	0	1337	329	1571	3236	1.369	0.335	265
	L-M-F15		0.150	0.010	401	71	0	1330	327	1564	3221	1.045	0.335	265
	L-H-F15	0.150		0.010	401	71	0	1355	334	1593	3282	1.369	0.335	243
	L-M-F30		0.150	0.015	330	142	0	1323	325	1554	3203	1.045	0.502	266
	L-H-F30	0.150		0.015	330	142	0	1348	332	1584	3265	1.369	0.502	243
	L-M-C30		0.150	0.005	401	0	71	1332	327	1564	3223	1.045	0.167	266
	L-H-C30	0.150		0.010	330	0	142	1357	334	1595	3285	1.369	0.335	243
	L-M-C15-F15		0.150	0.010	330	71	71	1327	325	1559	3211	1.045	0.335	266
	L-H-C15-F15	0.150		0.010	330	71	71	1352	332	1589	3273	1.369	0.335	243

Table 16. Fresh and hardened properties of concrete with cementitious material content of 280 kg/m^3(470 lb/yd^3)

a) SI Units

Cement Factor	**Mix ID**	**W/CM**	**Vol. of AGG**	**Yield**	**Air,** %	**Temp.,** F	**Fresh Density,** kg/m^3	**Slump,** mm		**Compressive Strength, MPa at the Age of**				
								0 min	1 h	1 day	3 days	7 days	28 days	360 days
280 kg/m^3 (470 lb/yd^3)	L-M	0.45	0.726	0.99	3.8	69	2390	18	0	9.9	16.7	28.1	36.4	44.0
	L-H	0.45	0.726	1.00	5.7	69	2367	40	2	11.2	24.8	31.7	36.8	45.6
	L-M-F15	0.45	0.722	0.98	4.7	71	2407	10	2	7.9	17.8	24.9	32.5	42.9
	L-H-F15	0.40	0.736	0.99	5.5	68	2402	5	0	11.2	23.0	32.9	36.5	44.2
	L-M-F30	0.45	0.718	0.99	6.1	68	2351	11	0	4.3	14.8	15.9	23.2	40.9
	L-H-F30	0.40	0.732	1.00	6.6	69	2363	9	0	8.5	16.9	22.6	29.7	45.3
	L-M-C30	0.45	0.723	0.99	6.2	69	2374	60	5	2.8	8.9	20.2	30.5	40.9
	L-H-C30	0.40	0.736	0.99	6.2	68	2394	23	0	6.9	22.7	33.2	43.8	47.3
	L-M-C15-F15	0.45	0.720	1.01	8.0	68	2327	50	15	4.7	13.6	18.4	23.9	39.1
	L-H-C15-F15	0.40	0.734	1.01	7.6	68	2343	64	0	5.4	19.0	19.8	33.4	47.7

b) US Customary Units

Cement Factor	**Mix ID**	**W/CM**	**Vol. of AGG Ratio**	**Yield**	**Air, %**	**Temp., F**	**Fresh Density,** lb/ft^3	**Slump, in**		**Compressive Strength, psi at the Age of**				
								0 min	1 h	1 day	3 days	7 days	28 days	360 days
280 kg/m^3 (470 lb/yd^3)	L-M	0.45	0.726	0.99	3.8	69	149	0.71	0	1436	2422	4076	5279	6382
	L-H	0.45	0.726	1.00	5.7	69	148	1.57	0.08	1624	3597	4598	5337	6614
	L-M-F15	0.45	0.722	0.98	4.7	71	150	0.39	0.08	1146	2582	3611	4714	6222
	L-H-F15	0.40	0.736	0.99	5.5	68	150	0.20	0	1624	3336	4772	5294	6411
	L-M-F30	0.45	0.718	0.99	6.1	68	147	0.43	0	624	2147	2306	3365	5845
	L-H-F30	0.40	0.732	1.00	6.6	69	148	0.35	0	1233	2451	3278	4308	6570
	L-M-C30	0.45	0.723	0.99	6.2	69	148	2.36	0.2	406	1291	2930	4424	5932
	L-H-C30	0.40	0.736	0.99	6.2	68	149	0.91	0	1001	3292	4815	6353	6860
	L-M-C15-F15	0.45	0.720	1.01	8.0	68	145	1.97	0.59	682	1973	2669	3466	5671
	L-H-C15-F15	0.40	0.734	1.01	7.6	68	146	2.52	0	783	2756	2872	4844	6918

3.3.4. Freezing and Thawing Resistance

The freezing and thawing resistance of investigated concrete is summarized in *Table 17* . After 300 cycles, all tested concrete types achieved a durability factor of more than 90% or higher and so passed the ASTM C666 benchmark of 60%.

Table 17. The durability of investigated concrete

Mix ID	**W/CM**	**Fresh Air,** %	**Surface Condition After Salt Scaling***	**Salt Scaling Mass Loss,** %	**F/T Mass Loss, %**	**F/T Durability Factor,** %
L-M	0.45	3.8	3	0.7	1.4	104
L-H	0.45	5.7	2	0.2	-	105
L-M-F15	0.45	4.7	4	2.1	-	106
L-H-F15	0.40	5.5	3	1.1	-	106
L-M-F30	0.45	6.1	5	4.7	1.9	102
L-H-F30	0.40	6.6	5	1.7	1.5	104
L-M-C30	0.45	6.2	2	1.2	1.3	97
L-H-C30	0.40	6.2	1	0.4	-	106
L-M-C15-F15	0.45	8.0	1	0.7	1.1	102
L-H-C15-F15	0.40	7.6	5	3.1	1.3	105

**Scale surface condition according to ASTM C672/C:*

0 – no scaling
1 – very slight scaling (3 mm [1/8 in.] depth, max, no coarse aggregate visible)
2 – slight to moderate scaling
3 – moderate scaling (some coarse aggregate visible)
4 – moderate to severe scaling
5 – severe scaling (coarse aggregate visible over entire surface)

Surprisingly, the worst, but acceptable, freeze-thaw durability results were recorded for concrete samples L-M-C30 with 30% of Class C fly ash. Overall, when tested up to 300 cycles, all the concrete samples except L-M-C30 demonstrated 3-6% increase of the durability factor. This can be explained by continuing hydration and strength development of the investigated concrete during the test.

Some loss of mass (less than 5%) due to scaling was observed for the investigated concrete (L-M-C30, L-M-F30 and L-M-C15-F15). The composition L-M-F30 demonstrated the most severe surface deterioration. As reported in *Table 17* and after

300 cycles of freeze-thaw, most concrete types had a small (about 1%) mass gain. This can be explained by the densification of structure due to ongoing hydration.

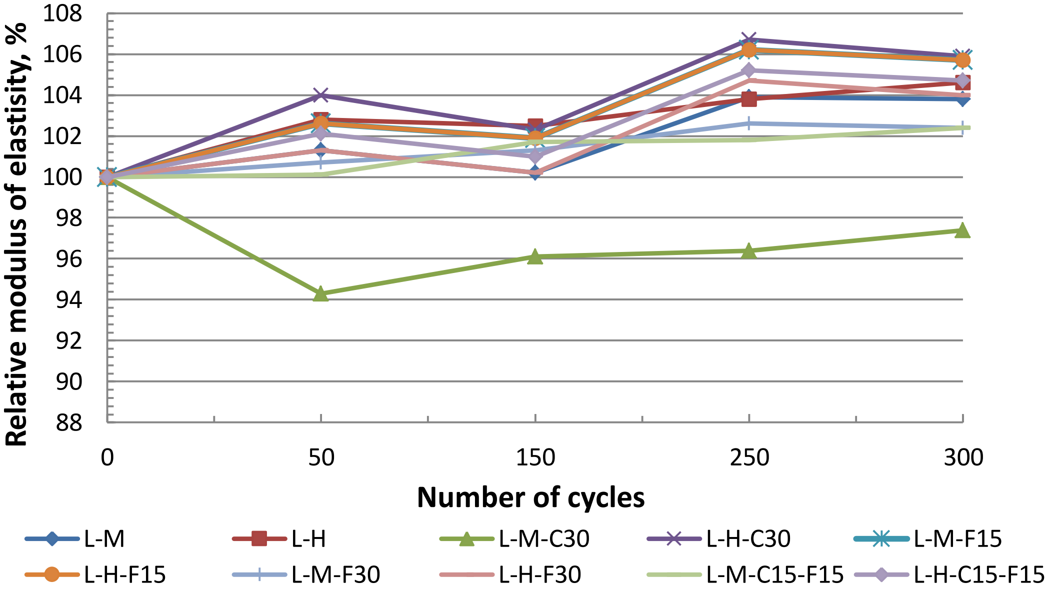


Figure 16. The change of the Durability Factor over freezing and thawing test

3.3.5. Salt-Scaling Resistance

The salt scaling resistance of the investigated concrete was assessed according to the standard C 672/C 672M-03 “Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals.” The visual condition of the surface was evaluated using a rating system according to the Standard C672/C-03. The results of the visual inspection were reported after each 10 cycles and up to 50 cycles (*Table 18*, *Figure 17, Figure 18, Figure 19, Figure 20, Figure 21*).

The results indicate that the reference concrete samples (L-M and L-H) and mixtures with 30 % Class C fly ash (L-M-C30 and L-H-C30) had the best salt scaling resistance considering the visual surface deterioration, which is also supported by a mass loss.

Table 18. The results of salt scaling test

Sample ID	Conditions of surface, after N cycles					Weight loss after 50 cycles, %
	10	20	30	40	50	
L-M	1	1	2	3	3	0.7
L-H	1	1	1	2	2	0.2
L-M-C30	2	2	2	2	2	1.2
L-H-C30	1	1	1	1	1	0.4
L-M-F15	4	4	4	4	4	2.1
L-H-F15	3	3	3	3	3	1.1
L-M-F30	5	5	5	5	5	4.7
L-H-F30	4	4	4	5	5	1.7
L-M-C15-F15	1	1	1	1	1	0.7
L-H-C15-F15	3	3	3	4	5	3.1

Figure 17. Concrete samples after 10 cycles

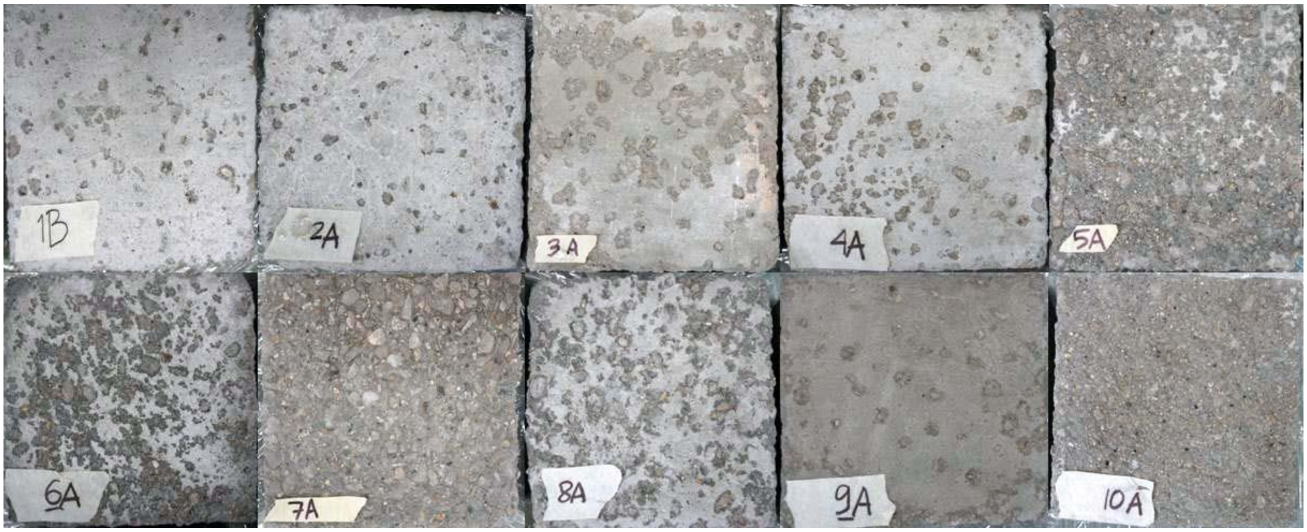


Figure 18. Concrete samples after 20 cycles

Figure 19. Concrete samples after 30 cycles

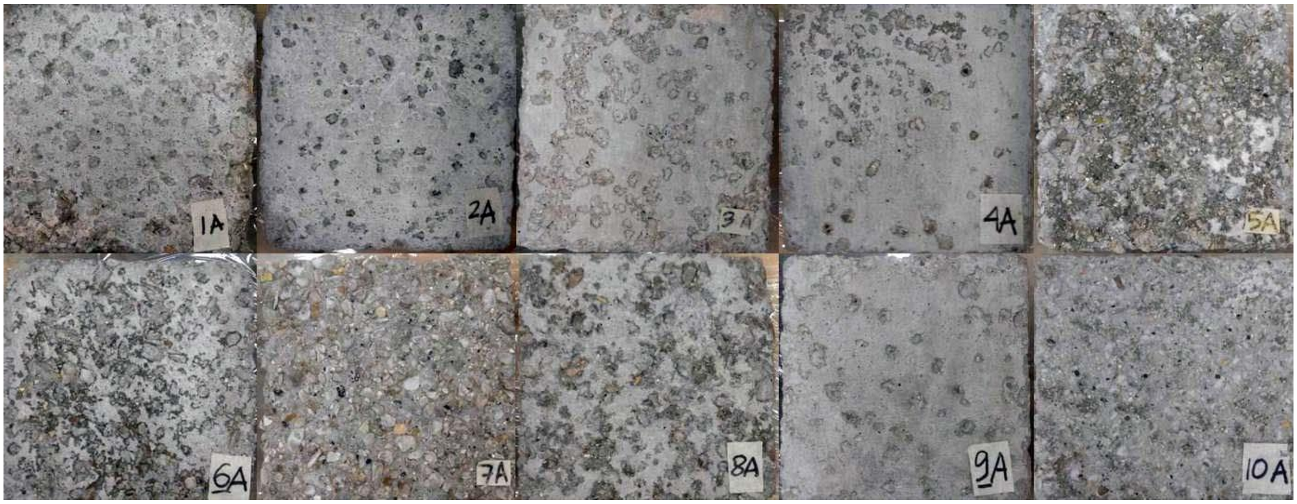


Figure 20. Concrete samples after 40 cycles

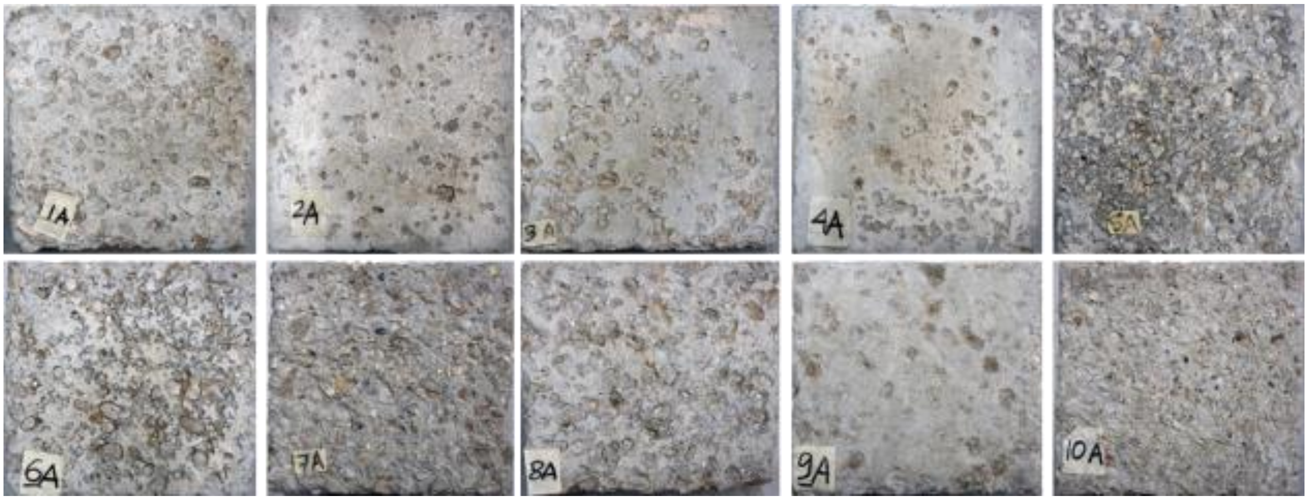


Figure 21. Concrete samples after 50 cycles

According to the mass loss results and visual appearance, the most deteriorated surfaces belong to the concrete samples containing up to 30 % of Class F fly ash (or a combination of two types of fly ash). The sample L-M-F30 with WR lost about 4.6% of the mass after 50 cycles of testing, and the sample L-H-C15-F15 had 3.1% mass loss. Even though the L-M-F15 composition had lesser visual surface deterioration (rated 4) in comparison with the mix L-H-F30, it demonstrated a more severe mass loss of 2.1%. Generally, due to higher W/C ratio all the samples with WR admixture had a lower salt scaling resistance in comparison with those containing HRWR admixtures. Importantly, all the compositions demonstrated a certain degree of surface deterioration after the first 10 cycles of freeze and thaw exposure.

It is important to note that the concrete sample L-M-C30 has very good surface scaling resistance with moderate mass loss; at the same time this composition demonstrated the lowest compressive strength. Surprisingly, the combination of Class C and F fly ash produced with WR admixture demonstrated a better behavior (with Rating 1) rather than the same concrete, but with HRWR admixture (Rating 5). This might be due to an excessive surface finish used for the composition with HRWR. All the concrete samples containing HRWR+AE admixtures had better strength, which can be correlated to better scaling resistance in chloride solutions. The only exception to this rule was observed for the samples L-H-C15-F15, which demonstrated slightly better strength, but severe surface scaling and high mass loss in comparison with the concrete L-M-C15-F15.

The Class C fly ash concrete had demonstrated a significantly better salt scaling resistance with very small weight loss and a Rating of ≤2. The opposite results were demonstrated by the concrete mixtures containing up to 30% of Class F fly ash, where a severe surface scaling was observed. Such difference in behavior can be related to the formation of the structure of the cementitious system and different chemical reactivity of fly ash, where Class F may need a longer time to develop an adequate microstructure to reduce the saturation. Segregation due to excessive finish and altering the air void structure near the surface can compromise the defense mechanism to this exposure. Overall, the salt scaling resistance was demonstrated by the reference compositions incorporating HRWR+AE or WR+AE admixtures.

4. CONCLUSIONS

This research demonstrated that concrete mixtures can be effectively designed by optimizing two essential phases comprising the material: the aggregates and cement paste. This project used the optimization of aggregates and chemical admixtures as established by the previous WHRP 0092-13-04 project. For this study, the cementitious material content was reduced to 280 kg/m^3 (470 lb/yd^3).

It was demonstrated that the heat of hydration can be used to evaluate the contribution of chemical admixtures combined with different types of fly ash and also to evaluate the setting time. The investigation of the mechanical performance of mortars was essential for the evaluation of various types of fly ash and effective combinations with chemical admixtures.

The use of PCE admixtures can enable up to 10 % reduction of W/CM ratio and water content vs. commonly used water-reducing admixtures under DOT specs. The PCE admixtures demonstrated an excellent compatibility with AE agents and various types of fly ash. As a result, fly ash can be effectively used in concrete with PCE at a cementitious material content of 280 kg/m^3 (470 lb/yd^3). The use of PCE admixtures and Class C fly ash combined enables the reduction of the W/CM ratio and, at the same time, enhances workability and improves performance. The combination of these two components works synergistically to enhance mechanical performance, resulting in compressive strength as high as 33.2 MPa (4,815 psi) at 28 days and above 47 MPa (6,816 psi) at 365 days. The use of Class F fly ash at the replacement levels up to 15% in concrete provides the strength levels similar to reference concrete; however, the use of PCE superplasticizer is required for an adequate strength development in concrete with more than 15% of Class F fly ash.

All investigated concrete mixtures had a relatively high air content (achieved by the application of AE admixture) and, therefore, excellent spacing factors and freeze-thaw resistance. However, the investigated concrete compositions had a very different salt-scaling performance. Specifically, only reference portland cement concrete and concrete with up to 30% of Class C fly ash had an acceptable salt scaling performance.

5. FUTURE RESEARCH

The various aspects of the reported research can be further extended:

- Better understanding of the effects of Class F fly ash on concrete performance and new methods for activation of Class F fly ash must be investigated.
- Further research is necessary to identify the effect of Class F fly ash on the composition and morphology of hardened cement matrix including time periods over 28 days.
- The investigation of the ASR mitigation of developed concrete with fly ash and fly ash combinations is necessary.

REFERENCES

1. *Report Card for America's Infrastructure*, 2013, ASCE.
2. Malhotra, V.M. and Mehta, P.K., *Pozzolanic cementitious materials.* Advances in Concrete Technology, 1996. vol 1(Gordon and Breach, London): p.11.
3. Sobolev, K. and Ferrada-Gutiérrez, M., *How Nanotechnology Can Change the Concrete World: Part 2.* American Ceramic Society Bulletin, 2005. No. 11: pp. 16-19.
4. Li, G., *Properties of high-volume fly ash concrete incorporating nano-*SiO_2. Cement and Concrete Research, 2004. 34: p. pp.1043-1049.
5. Collepardi, M., Skarp, U., and Troli, R. *Optimization of Silica Fume, Fly Ash and Amorphous Nano-Silica in Superplasticized High-Performance Concretes*. in *8th CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag , SP-221*. 2004. Las Vegas, USA.
6. Celik, O., Damci, E., and Piskin, S., *Characterization of fly ash and it effects on the compressive strength properties of Portland cement.* Indian Journal of Engineering and Materials Sciences, 2008. 15(5): p. 433.
7. Thongsanitgarn, P., Wongkeo, W., Chaipanich, A., and Poon, C.S., *Heat of hydration of Portland high-calcium fly ash cement incorporating limestone powder: Effect of limestone particle size.* Construction and Building Materials, 2014. 66: p. 410-417.
8. Sobolev, K., Zhiblin, L., Flores-Vivian, I., and Pradoto, R., *Nano-Engineered Cements with Enhanced Mechanical Performance.* Journal of the American Ceramic Society, 2015. 1-9.
9. Lin, Z., Sobolev, K., and Flores-Vivian, I. *Nano-Engineered Cements with Improved Early Strength*. in *4th International Symposium on Nanotechnology in Construction 4 (NICOM4)*. 2012. Greece, May 20-22.
10. Naik, T.R., Ramme, B.W., and Tews, J.H., *Pavement construction with high-volume Class C and Class F fly ash concrete.* ACI Materials Journal, 1995. 92(2): p. 200-210.
11. Naik, T.R., Kraus, R.N., Ramme, B.W., and Siddique, R. *Mechanical properties and durability of concrete pavements containing high volume fly ash*. in *6th CANMET/ACI International Conference on Durability of Concrete*. 2003. Thessaloniki, Greece.
12. Rangaraju, P.R. and Sompura, K.R. *Influence of Cement Composition on Expansions Observed in Standard and Modified ASTM C1260 Test Procedures*. in *Transportation Research Record No. 1914: Concrete Materials*. 2005.
13. Tikalsky, P., Schaefer, V., Wang, K., Scheetz, B., Rupnow, T., Clair, A.S., Siddiqi, M., and Marquez, S., *Development of Performance Properties of Ternary Mixes: Phase I Final Report*, 2007, FHWA Pooled Fund Study TPF-5. p. 117.

14. Tikalsky, P., Schokker, A., and Tepke, D., *Potential Concrete Mixture Designs for the I-99 Corridor, Report No.: FHWA-PA-2002-040-97-04*, 2003, Pennsylvania Department of Transportation.

15. La Barca, I.K., Foley, R.D., and Cramer, S.M., *Effects of Ground Granulated Blast Furnace Slag in Portland Cement Concrete – Expanded Study, Final Report, Project ID: 0092-05-01*, 2007, Wisconsin Highway Research Program, WisDOT.

16. Collepardi, S., Coppola, L., Troli, R., and Collepardi, M., *Mechanisms of Actions of Different Superplasticizers for High-Performance Concrete*, 1999.

17. Sakai, E., Yamada, K., and Ohta, A., *Molecular Structure and Dispersion-Adsorption Mechanisms of Comb-Type Superplasticizers Used in Japan.* Journal of Advanced Concrete Technology, 2003: p. 16-25.

18. Bentz, D.P., *Powder Additions to Mitigate Retardation in High-Volume Fly Ash Mixtures.* ACI Materials Journal, 2010. 107: p. 508-514.

19. Fennis, S.A. and Walraven, J.C., *Using particle packing technology for sustainable concrete mixture design.* Heron, 57 (2012) 2, 2012.

20. Fennis, S., *Design of ecological concrete by particle packing optimization*2011: TU Delft, Delft University of Technology.

21. American Society for Testing and Materials ASTM C989, *Standard Specification for Slag Cement for Use in Concrete and Mortars.*

22. American Society for Testing and Materials ASTM C618, *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*, 2003.

23. Hover, K.C., Folliard, K.J., Ley, M.T., and Harris, N.J., *The Use of the Foam Index Test to Predict AEA Dosage in Concrete Containing Fly Ash: Part I—Evaluation of the State of Practice.* Journal of ASTM International, 2008. 5(7): p. 1-15.

24. Wang, K., Ge, Z., Grove, J., Ruiz, J.M., Rasmussen, R., and Ferragut, T., *Developing a simple and rapid test for monitoring the heat evolution of concrete mixtures for both laboratory and field applications.* 2007.