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Evaluation, Beneficiation, and Implementation of Alternative Concrete Pozzolans for Transportation Infrastructure

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16. Abstract

The supply of conventional supplementary cementitious materials (SCMs such as coal fly ash and ground granulated blast furnace slag) continues to fall further behind the concrete industry's demand to produce durable and sustainable concretes. As an alternative, interest in nontraditional pozzolanic materials continues to grow. This study evaluated two such alternatives: fluidized bed combustion (FBC) fly ash and impure calcined clay. Four compositionally different FBC fly ashes and one low-purity kaolinite clay deposit, all from the Mid-Atlantic region of the United States, were evaluated. These pozzolans were characterized according to the requirements of ASTM C618 (equivalent with AASHTO M 295), "Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete." Additionally, these pozzolans were used at 20% mass replacement of portland cement in a pavement-grade concrete mixture and their effects on the fresh, hardened, and durability properties of the concrete were evaluated. It was observed that desirable slump, air content, air-voids structure, and strength development can be achieved in concrete with FBC fly ashes and calcined clays. In addition, the use of these pozzolans improved the durability of concrete with respect to chloride penetration, alkali-silica reaction, and drying shrinkage in comparison with a control (100% portland cement) mixture. A preliminary cost analysis and suggestions for modifying ASTM C618 to better regulate these pozzolans are offered.

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CHAPTER 1

Introduction

BACKGROUND

Pozzolans or supplementary cementitious materials, SCMs (such as coal fly ash and ground granulated blast furnace slag), are a key ingredient of today's concrete mixtures, as they improve the workability, sustainability (e.g., embodied energy and CO_2 footprint), and long-term durability (e.g., against corrosion, alkali-aggregate reaction, and sulfate attack) of concrete [1]. SCMs also reduce the lifecycle cost of concrete by providing potential materials cost-savings while reducing the maintenance needs of concrete structures.

Recently, the availability and quality of conventional SCMs have been a source of concern nationwide, and this is forecasted to become more severe in the future. For instance, pulverized coal (PC) fly ash production in the United States has declined by more than 50% since 2008 due to coal power plant retirements and conversion to natural gas fuel (see **Figure 1**) [2]. Based on the current practices, it is estimated that by the year 2030, the supply of ASTM C618-compliant freshly produced fly ash in the United States will remain at ~14 million tons per year, while the demand will exceed ~35 million tons per year [3]. In addition, stricter air emission regulations have resulted in fly ashes with higher carbon, alkali, and sulfur contents, which are not usable in concrete without extensive beneficiation. A recent survey by the AASHTO subcommittee on materials [4] of all state Departments of Transportation (DOTs), the Federal Aviation Administration (FAA), and the Army Corps of Engineers showed that over 80% of the respondents had issues with fly ash availability over the four-year scope of that study.
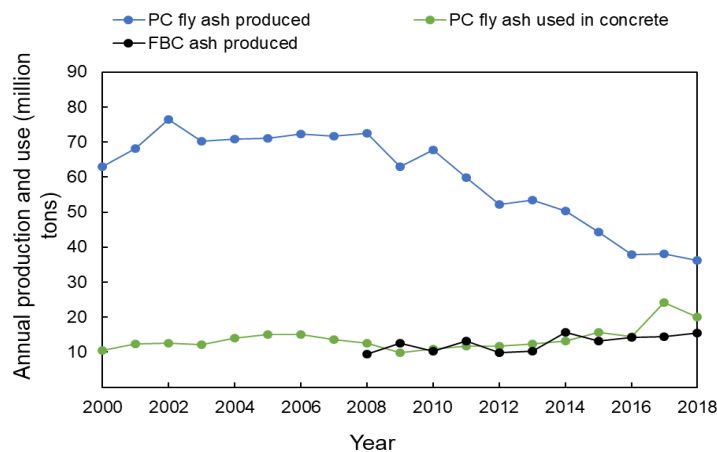
Figure 1. Statistics on the production and utilization of pulverized coal and fluidized bed combustion fly ash (data from [2])

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Ground granulated blast furnace slag (GGBFS) is facing even more severe supply challenges, as North America primarily relies on imports from Europe and Asia, and the total world supplies of slag is less than 5% of the amount of cement clinker produced [5,6]. Unless addressed, the SCM shortage presents an insurmountable challenge to concrete producers and transportation agencies to deliver and build with high-quality and durable concrete at a sustainable cost to taxpayers, specifically in the era of shrinking public funding for infrastructure renovation. As such, there is a significant and urgent need to identify, evaluate, and commercialize new SCM sources for concrete construction.

One resource that may prove to be an acceptable, available, and low-cost alternative SCM is coal-based fluidized bed combustion (FBC) fly ash. Despite large available quantities (**Figure 1**), FBC fly ash is currently not implemented in concrete production since its properties and performance are not sufficiently known. This in part has led to the exclusion of FBC fly ash from the scope of common standard specifications for fly ash for use in concrete, such as ASTM C618 [7] and AASHTO M 295 [8]. To address this deficiency, the present research intends to improve the understanding of FBC fly ash and its impact on concrete performance. Calcined clay is another alternative SCM that may have a high potential for use in concrete. Impure kaolinite clays are abundant in many regions of the world (e.g., in the Mid-Atlantic and Southeastern United States) and may prove to be an ideal pozzolanic material to deliver high-quality concrete at a low cost. This study investigates one such clay source for its properties and performance in concrete.

LITERATURE REVIEW

Fluidized Bed Combustion Fly Ash

FBC is a combustion technology suitable for burning extremely low-grade coal (i.e., refuse coal) for power generation, with the environmental benefit of cleaning up waste coal (culm or gob) piles that produce acid mine drainage (AMD) [9]. FBC boilers use sulfur-absorbing materials such as ground limestone as kiln feed, and operate at lower combustion temperatures (750 °C to 900 °C) compared to conventional PC boilers that operate at 1150 °C to 1750 °C. This reduces harmful acid gas (SO_x and NO_x) emissions. However, the resulting anhydrite ($CaSO_4$) is collected comingled with fly ash. As such, FBC fly ash tends to have an elevated sulfur (SO_3) content, especially if a high-sulfur coal was burned, and this may lead to reduced workability, false set, and a risk of volume instability in concrete due to ettringite formation [10]. In addition, sub-optimal operation of FBC boilers may result in fly ash with elevated loss-on-ignition (LOI) due to its residual unburned carbon content [11,12], which can impact the workability and air entrainment of concrete mixtures [13,14]. Due to lower combustion temperature of FBC boilers, the mineral matter (e.g., clays) in coal does not melt but is dehydroxylated, resulting in high surface area calcined materials with poor crystallinity. This may result in high water demand, yet good pozzolanic reactivity [15]. It must be mentioned that a common type of FBC boilers is the circulating fluidized bed combustion (CFBC) technology, which creates a rapid recycling loop of fuel particles to enable their near-complete combustion, thereby improving the combustion efficiency [16].

Systematic studies on the performance of concrete containing FBC fly ash are scarce. Most of the available literature reports on the impact of FBC fly ash on the mechanical properties of concrete (e.g., compressive strength and modulus of elasticity). While some such studies have shown improvements in concrete strength with the use of FBC fly ash pozzolan [17,18], others have reported otherwise [19,20]. Very few studies have evaluated the effects of FBC fly ash on concrete durability. Chi and Huang [21] examined a CFBC fly ash with very high contents of free lime and SO_3, making it unusable for use as a sole pozzolan in concrete. Instead, they evaluated blends of class F pulverized coal fly ash and the CFBC fly ash at mass ratios of 1.5 and 2.5 (PC to CFBC). They reported that the blended fly ashes reduced the water and chloride permeability of concrete and increased the resistance to sulfate attack, but also increased concrete susceptibility to carbonation. Jóźwiak-Niedźwiedzka [22] reported lower chloride diffusion coefficient and higher electrical resistivity for concretes containing 15% or 30% CFBC fly ash as cement replacement. She also observed an improved scaling resistance with 15% CFBC fly ash, but at 30% the scaling resistance declined. Similarly, Glinicki and Zielinski [23] showed that using 20%, 30%, or 40% CFBC fly ash worsened the de-icing salt scaling of concrete, and the negative effects were proportional with the dosage of CFBC fly ash and its unburned carbon content. Further information about FBC fly ash and its performance in concrete can be found at literature [15,24,25].

Impure Calcined Clay

High-purity kaolinite calcined clay, also known as metakaolin (MK), has been utilized in the concrete industry as a high-quality pozzolan for the last two decades. MK is produced by calcining high-purity (95%+ by mass) kaolinite clay with little to no iron oxides to ensure a white color product. Research has proven that MK improves the early- and later-age strength and durability of concrete [26-29]. However, MK is expensive (costing on average 3× more than portland cement) and its sources are limited. As such, it has become a premium pozzolan that is used for certain niche applications. Impure kaolinite clay sources, on the other hand, are abundant, especially in the Mid-Atlantic and Southeastern United States, as well as many other regions in the world. As shown in **Figure 2**, Ulitosols (orange color) and Oxisols (red color) are rich in kaolinite and are abundant in large areas of the United States. These clays are formed from long weathering processes in hot rainy climates, resulting in a clay-rich soil dominated by quartz, kaolinite, and iron oxide minerals [30,31]. Limited literature is available on impure calcined clays and their performance in concrete. It has been recently reported that clays containing as low as 40% kaolinite may be used to produce acceptable pozzolans for concrete and at a low cost (~50% of the cost of portland cement) [32]. There is a significant need to characterize low-purity resources (common clay deposits, soils) and evaluate their performance in concrete and also to provide more reliable information for concrete producers.

There are three common groups of clay minerals: kaolinite, montmorillonite-smectite, and illite-micas [26]. Among them, kaolinite has the greatest potential to be used as SCM due to its bi-layer t-o structure (a silica tetrahedra layer connected to an alumina octahedra later), with hydroxyl groups connected to the octahedral layer and located at the interface between adjacent repeat t-o units [28]. This facilitates thermal activation (i.e., calcination) of kaolinite at lower temperatures, leading to a partial or complete breakdown of the clay structure by removing OH^- groups (i.e., the dehydroxylation process) and producing a highly reactive pozzolan [29]. In contrast, in smectite and illite clays, OH^- groups are located at the middle of individual tri-layer t-o-t units and this mitigates dehydroxylation.

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The optimum calcination temperature of kaolinite has been reported to be in the range of 650–850 °C depending on its composition and availability of flux agents [29,32-34]. Calcination produces a poorly crystalline aluminosilicate compound, which is metastable and can dissolve in the alkaline pore solution of concrete. Most commonly, calcined clays can react pozzolanically with calcium hydroxide (CH) and produce calcium (alumino-)silicate hydrate (C-S-H and C-A-S-H), serving as the major binder phase in concrete. Other reaction products of calcined clays in concrete include hemi- and mono-carboaluminate AFm phases ($C_4A\bar{C}H_{11}$ and $C_4A\bar{C}_{0.5}H_{12}$) and calcium aluminate hydrates (C_4AH_{13} and C_3AH_6) [33,35,36]. Here, cement chemistry notations are used where C, S, A, H, and $\bar{C}$ represent CaO, SiO_2, Al_2O_3, H_2O, and CO_2, respectively.
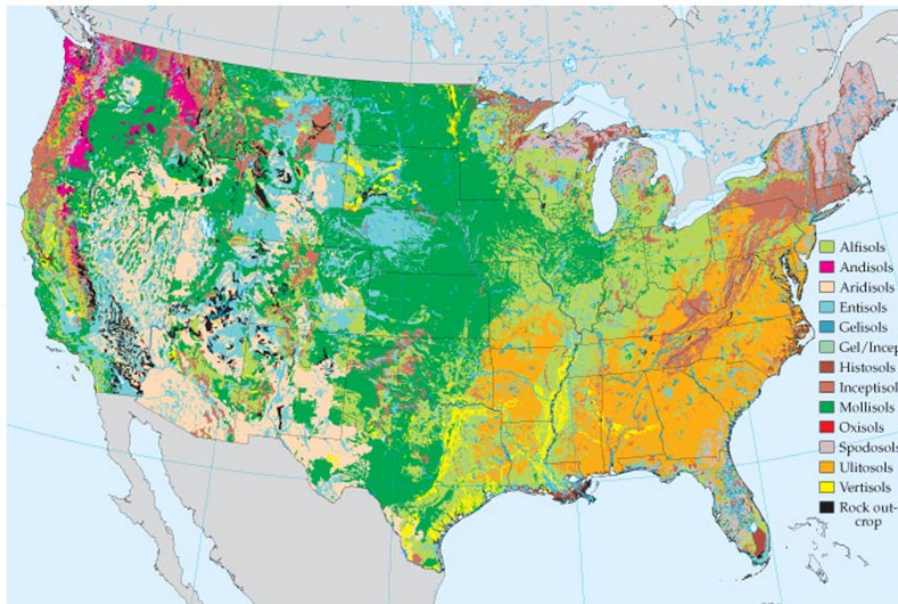
Figure 2. Location of impure kaolinite sources in the United States [30]

The maximum replacement level of portland cement with calcined clays is reported to be approximately 30% by weight. This limit is not due to complete consumption of portlandite (CH). Rather, it is due to the negative impact of calcined clays on the workability of concrete [37], and this cannot be fully counteracted by the use of water-reducing admixtures (WRA), as the required WRA dosage may exceed the recommended limit by the admixture manufacturer and such a high dosage may severely impact the setting and strength development of concrete [38]. Past research has shown that the use of calcined clay can improve the mechanical properties (i.e., the compressive, tensile, and flexural strength) and durability of concrete [27,36-40]. Some studies [26,27,35,37] reported that calcined clay is quite effective in enhancing the early- and later-age strength of concrete. Moreover, calcined clay has been demonstrated to improve the resistance of concrete against sulfate attack and chloride ion penetration [37]. The water requirement to achieve normal consistency was found to depend on the type and fineness of clay minerals and their degree of dehydroxylation [37,41].

Over the last few decades, a large number of studies have been performed on the activation of raw clays [42,43], optimization of calcination protocol for pure kaolinite [41,44], and evaluating the

effect of metakaolin on the properties of concrete [36,44]. As mentioned earlier, the abundant clay deposits include a mixture of kaolinite and other clay minerals plus impurities such as quartz and iron oxide [33]. In this study, an impure source clay (SC) as a by-product of a large commercial aggregate production facility is examined, calcined, and used in a portland cement concrete mixture to evaluate its properties and performance.

OBJECTIVES

The objective of this study was to evaluate, improve, and facilitate the use and field implementation of two new, low-cost, and locally available SCM sources that can be used for producing high-performance concrete. First is the fluidized bed combustion fly ash that is widely produced (3+ million tons/year) in Pennsylvania and West Virginia as a result of environmental cleanup of waste coal piles in the region by FBC electric power utilities. Second is a low-purity kaolinite clay that is intermixed with glacial deposits of sand and gravel within the region (PA, MD, VA). While they are cheap and locally abundant, these SCM resources have not been previously used in concrete, their properties and performance are largely unknown, and as such, they are not included in DOT specifications in the region. This study will address these gaps by providing reliable data on complete characterization of these materials and their performance in concrete mixtures. Suggestions for revising the prevailing agency specifications are made to allow a safe and effective use of these novel pozzolans.

CHAPTER 2

Methodology

INTRODUCTION

This chapter of the report describes the acquisition of each alternative pozzolan—including four FBC fly ashes and one impure kaolinite clay—that were the subject of this project. Methods for pre-processing of the pozzolans are described, including purification and calcination of the clay. In addition, the chapter provides a clear and precise description of the experiments conducted to characterize the physical and chemical properties of each pozzolan and to evaluate their performance in concrete mixtures.

POZZOLAN ACQUISITION AND PROCESSING

Acquiring Fluidized Bed Combustion Fly Ashes

Four fly ashes from CFBC power plants in Pennsylvania were acquired. Two fly ashes were produced by combustion of anthracite (Ant.) coal while the other two fly ashes were produced by combustion of bituminous (Bit.) coal. Anthracite is the highest rank coal and has low SO_3 content, resulting in a fly ash with low SO_3 and CaO. Bituminous coal is the most abundant form of coal in the world and has high SO_3 content, resulting in a fly ash with high SO_3 and CaO. Bituminous coal accounted for 46% of the total U.S. coal production in 2017 [45]. Anthracite culm piles exist in Eastern Pennsylvania while bituminous gob piles are abundant in Western Pennsylvania and West Virginia (**Figure 3**). Information about the current refuse coal burning FBC power plants in the region is available through ARIPPA [46].

Acquiring Calcining Clay

ASTM and AASHTO specifications for concrete aggregates (ASTM C33-18, AASHTO M 6, and AASHTO M 80) place a limit on the maximum allowable fines (particles smaller than #200 sieve) that can be included in aggregates. To meet this limit, aggregate producers often need to wash their aggregates to remove dusts and fines. This practice results in a washout slurry that needs to be properly treated and recycled or disposed of. In this study, the aggregate washout slurry from a large sand and gravel pit in Maryland was investigated. The pit produces ~700 tons/day of by-product fines (dry weight), which were believed to primarily contain clay minerals.

A 275-gallon sample of the washout slurry (<5% solid content) was acquired. The solids were allowed to settle naturally, and the resulting mud was dried in an oven at 110 °C for 24 hours and then ground to pass sieve #18 (1.00 mm). The resulting SC was calcined at a heating rate of 8

°C/min up to a maximum temperature of 750 °C (approximately half of the required temperature for producing portland cement clinker). The residence time at maximum temperature was 3 hours. The clay was then allowed to cool down to room temperature within 15 minutes. The resulting calcined clay (CC) was milled for 2 hours in a ceramic ball mill to produce a desired level of fineness (<34% retained on #325 sieve) while meeting ASTM C618's water requirement limit of 115% maximum.
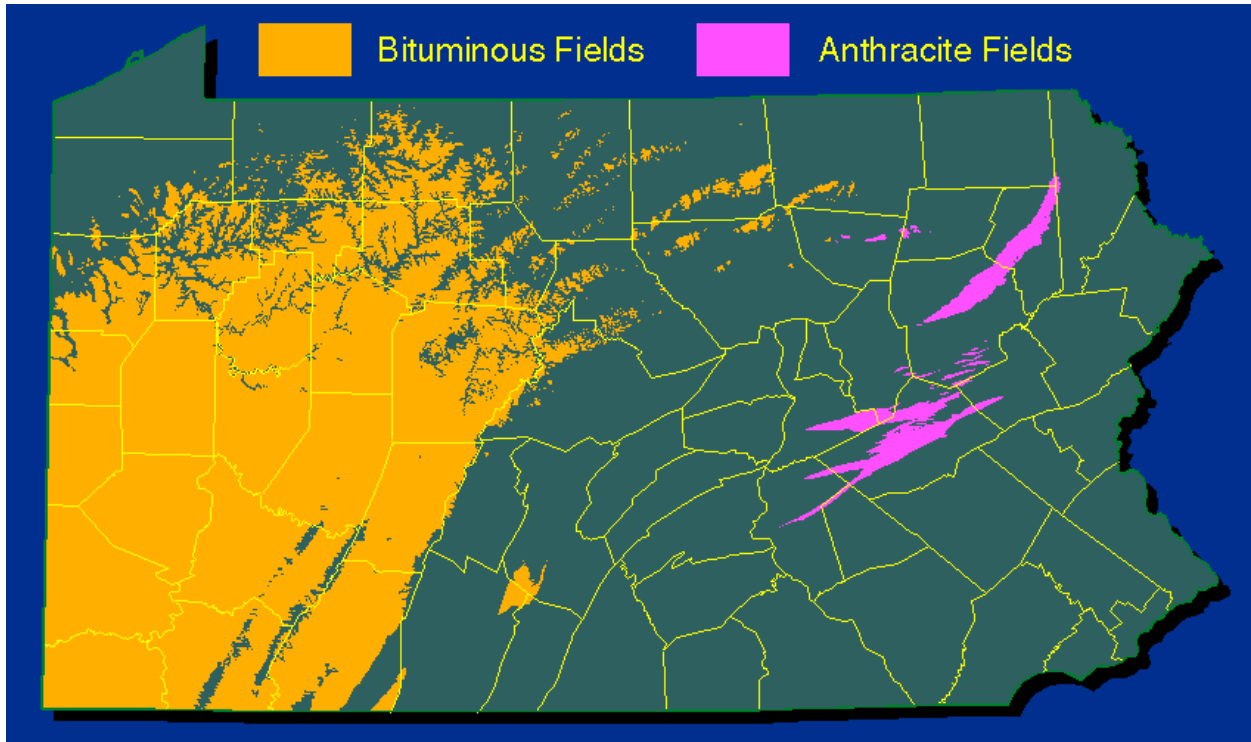
Figure 3. Distribution of coal ranks within Pennsylvania [47]

Purification of Source Clay

Based on the results of quantitative X-ray diffraction (QXRD), presented in the next chapter, it was determined that approximately 50% of the source clay is made of mineral quartz (SiO_2), which is non-reactive in concrete. As such, and to improve the pozzolanic reactivity of the resulting calcined clay, a number of purification methods were applied to separate the quartz fraction and enhance the kaolinite content of the clay. These methods were based on dispersant-assisted sedimentation of clay slurries, in which clay agglomerates are dispersed in water by use of a deflocculating agent, which gives a positive surface charge to clay particles. This results in electrostatic repulsion and dispersion of clay particles away from larger quartz particles. The latter settles out of the slurry by a gravitational or centrifugal force. A number of deflocculating agents were tested, including:

- Sodium hexametaphosphate, $(NaPO_3)_6$, abbreviated as SHMP;
- Sodium carboxymethyl cellulose, abbreviated as SCMC;
- Sodium polyacrylate, $(C_3H_3NaO_2)_n$, abbreviated as SPA; and

- Sodium metatungstate, $H_2Na_6O_{40}W_{12}$, abbreviated as SMT.

A range of deflocculant concentrations and pH values were examined. For the purification, 50 gr of oven-dried source clay was added to 125 mL water containing the deflocculant at a target concentration. The resulting slurry was vigorously mixed for 2 minutes in a high-shear mixer. Then, the slurry was poured into a graduated cylinder and the cylinder was filled with distilled water until it reached the 1,000 ml mark. To adjust the pH of the slurry, NaOH or HCl solutions were used instead of distilled water in this step. The cylinder was turned upside down several times to have a good mix of the slurry and the added water. The settlement of quartz particles was monitored for a period of 24 hours.

It was observed that SHMP and SCMC were most effective in dispersing clay particles, while SPA and SMT did not produce effective separation. Also, neutral pH levels were found to be most effective. As shown in **Figure 4**, more concentrated layers of quartz (light brown) and iron oxide (dark brown) form at the bottom of SHMP cylinders in comparison with those in the SCMC cylinders. Further tests were performed to minimize the required dosage of SHMP to reduce the cost and the contamination level (e.g., by Na, P, etc.) in the resulting purified clay. **Figure 5** provides a comparison of the sedimentation experiment performed using 0.05% to 4.0% SHMP solutions. Visual observation of the height and color of the sedimentation layers reveals that 0.05% and 0.1% SHMP were not effective enough to disperse the clay particles, as some sedimented together with quartz. Further, the height of the sedimented quartz layer in the cylinder with 0.25% SHMP solution was lower than that in cylinders containing higher deflocculant dosages. As such, it was determined that SHMP at 0.5% provides the optimum clay purification. In other words, the optimum purification method involved using 12.5 g SHMP per 1 kg of source clay and producing a slurry with 5% clay content. After 24 hours of sedimentation, the suspension portion was removed, dried, and calcined (using the aforementioned protocol) to be produced a purified calcined clay (PCC).
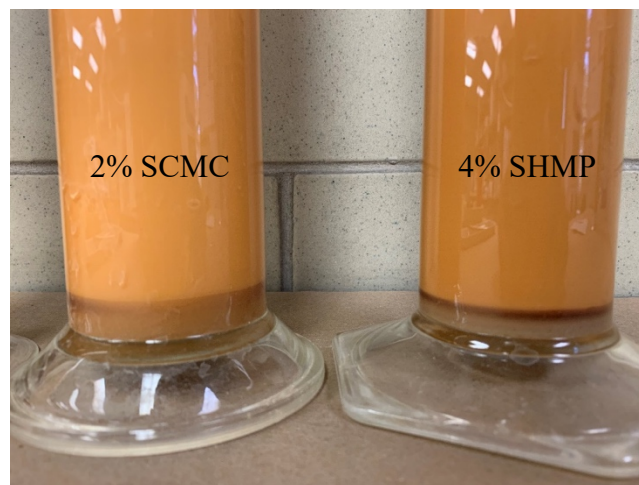
Figure 4. Sedimentation experiment to separate quartz from clay by using SHMP and SCMC deflocculants
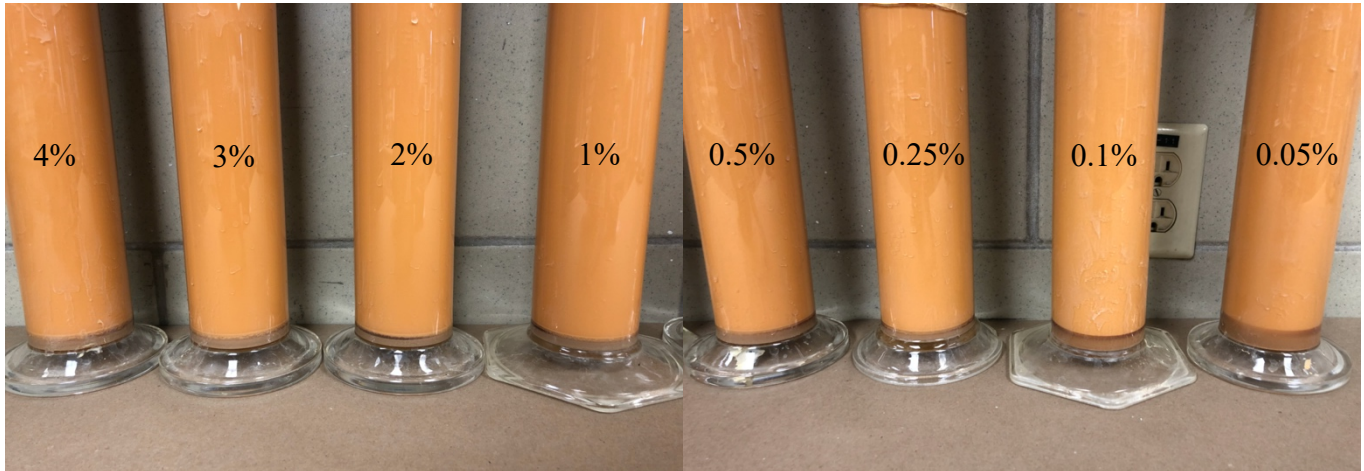
Figure 5. Using different concentrations of SHMP to disperse the clay particles and promote separation of quartz (after 24 hours)

POZZOLAN CHARACTERIZATION AND TESTING

ASTM C618 Characterization of Each Pozzolan

The physical properties as well as the chemical and mineralogical composition of each pozzolan were evaluated and compared with the specification limits in ASTM C618-19 for fly ash and for natural pozzolans. Physical property tests included the moisture content (ASTM C311-17), fineness (ASTM C430-17), particle size distribution (using laser diffraction), density (using helium pycnometry), loss on ignition (ASTM C311-17), carbon and sulfur contents (using infrared spectroscopy), water requirement (ASTM C311-17), strength activity index (ASTM C311-17), and soundness (ASTM C151-18).

In addition, the chemical and mineralogical compositions of the pozzolans were determined via X-ray fluorescence spectroscopy (XRF) and X-ray diffraction (XRD). One sample per material was tested for each XRF and XRD. For XRF, a small portion of each material was mixed with lithium borate flux and heated up to 1,000 °C. The resulting glass bead was analyzed using XRF. Quantitative XRD with Rietveld refinement was performed to identify and quantify the mineral and amorphous phases present in each material. Samples were ground to pass sieve #400, mixed with 15% internal standard (ZnO), and placed on a spinner stage rotating at 4 rev/s. The incident X-ray beam was Cu Kα radiation at 45 kV and 40 mA. Incident settings were: 0.125° divergence slit, 0.25° anti-scatter slit, 0.04 rad. Söller slits, and 15 mm beam mask. Diffracted settings were: 0.125° receiving slit, 0.04 rad. Söller slits, and 0.02 mm nickel filter. Diffraction patterns were collected over the range 5-70° 2θ with step size of 0.02°, for a total duration of ~30 minutes. A PIXcel detector in scanning line mode was used.

Scanning electron microscopy (SEM) was used to obtain 2D (polished surface) images of SC, CC, and PCC powder as well as two of the FBC fly ashes. Each sample was prepared using a mixture of epoxy with pozzolan powder (1:1 by weight). The resulting material was poured into a cavity inside a molded epoxy disk with the diameter of 25 mm and height of 12.5 mm [48]. After the

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epoxy had set, the sample was polished to 0.25 µm and carbon coated. Imaging was performed at 1,000× magnification using a 15 kV, 2nA electron beam. A working distance of ~10 mm was used.

Laser diffraction particle size distribution (PSD) testing was conducted by measuring the angular variation in the intensity of light scattered as a laser beam passed through a well-dispersed sample in water. A small amount (~0.03 g) of pozzolan was added to distilled water and the sample was sonicated for 1 min before PSD testing. The particle size distribution was computed using a refractive index of 1.6 and absorption coefficient of 1.0.

In addition to the standard LOI test, infrared spectroscopy using a Leco analyzer was used to measure the total carbon (organic and inorganic) and sulfur contents in each pozzolan. In this technique, the sample was combusted in air up to 1,450 °C inside the analyzer furnace, and the emitted CO_2 and SO_2 gases were measured separately using infrared detectors.

Performance of the Pozzolans in Mortar and Concrete Mixtures

The strength activity index (SAI) of each pozzolan was measured after 7 and 28 days of curing in saturated limewater, in accordance with ASTM C311-17. The control mortar was prepared with w/c = 0.484, using a type I/II portland cement and standard sand with the absorption capacity of 0.58%. In the test mixture, 20% of cement was replaced with each pozzolan and enough water was added to reach a flow of ± 5% of that of the control mixture (flow was measured according to ASTM C1437-15). Mixture proportions are provided in **Table 1**.

Table 1. Mixture design for SAI testing of each pozzolan

Specimen	Cement (g)	SCM (g)	Standard sand (g)	Water (g)	WRA (mL/100 kg cementitious)	Flow (%)	w/cm
Control mix	500	0	1,375	242	0	90	0.484
Ant.1 FBC	400	100	1,375	265	0	90	0.530
Ant.2 FBC	400	100	1,375	250	0	90	0.500
Bit.1 FBC	400	100	1,375	265	0	90	0.530
Bit.2 FBC	400	100	1,375	258.7	0	90	0.517
CC	400	100	1,375	273.5	0	85	0.547
PCC	400	100	1,375	278.3	0	85	0.557

Based on the results of the above tests, two FBC fly ashes (Ant. 1 and Bit. 1) as well as two calcined clays (CC and PCC) were selected and further evaluated using mortar and concrete tests. These tests are summarized in **Table 2** and the mixture proportions of each mortar and concrete mixture are provided in **Tables 3**, **4**, and **5**. All of the mortars were prepared according to ASTM C305-14 protocol, while the concrete mixtures were prepared according to ASTM C192-19.

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Table 2. Mortar and concrete tests performed on selected pozzolans

Test	Purpose (to measure the impact of each pozzolan on…)
Mortar Tests	
Setting time (ASTM C403-16)	the time of setting of standard mortars
Volume stability (ASTM C157-17, C1038-14b)	the susceptibility of each mortar to drying shrinkage and expansion under water
Sulfate attack (ASTM C1012-18b)	the resistance against external sulfate attack
ASR (ASTM C1567-13)	mitigating alkali silica reaction (ASR)
Concrete Tests	
Slump (ASTM C143-15a)	the workability of concrete
Unit weight and plastic air content (ASTM C138-17a, C231-17a)	the density and air content of fresh concrete
Cylinder compressive strength (ASTM C39-18)	the compressive strength of concrete at 7, 28, and 56 days
Hardened air structure (ASTM C457-16)	the volume fraction and spacing of air voids in hardened concrete
Ion penetrability (ASTM C1202-18)	ion transport in concrete
Water sorptivity (ASTM C1585-13)	moisture transport in concrete

Mortar mixtures were prepared and tested to evaluate the impact of each pozzolan on the time of setting, volume stability, resistance to external sulfate attack, and resistance against alkali-silica reaction (ASR). The mixture proportions for these mortars are provided in **Table 3**. All of the mortars with the exception of the ASR mortars contained 20% by mass of pozzolan as a replacement of portland cement.

The time of setting of the mortars was tested using the penetration resistance method (ASTM C403-16). Mortar mixtures were poured into cylinder molds (150×150 mm), capped, and stored at 23 °C and 100% RH. The penetration resistance of fresh mortars was recorded until it reached 3.45 MPa (500 psi) and 27.58 MPa (4,000 psi) for the initial and final setting time, respectively. Three replicate specimens of each mixture were measured. For FBC fly ashes, the mortars were obtained by wet sieving the corresponding concrete mixtures (**Table 4**) through a #4 sieve to remove the coarse aggregates. However, for calcined clays CC and PCC, mortar mixtures were prepared using the proportions in **Table 3b** and these mortars were used for measuring the setting time and drying shrinkage. These mortars had the same w/cm = 0.484 as the control mortar. A sufficient dose of WRA (MasterGlenium 7620 by BASF) was added to achieve a similar flow (90%±5%) in the test mortars in comparison with the control.

Table 3(a). Mixture proportions for ASR testing of mortars containing FBC fly ash

Mortar	Highly reactive R2 sand (gr)	Cement (gr)	FBC Fly ash (gr)	Water (gr)	Flow (%)
Control (100% OPC)	1,350	600	0	282	-
20% Ant./Bit.	1,350	480	120	282	-
30% Ant./Bit.	1,350	420	180	282	-
40% Bit.	1,350	360	240	282	-
Mortar	Sand (gr)	Cement (gr)	FBC Fly ash (gr)	Water (gr)	Flow (%)
Control	2,074.5	750	0	352.5	88
20% Ant.	2,074.5	600	150	397.5	86
20% Bit.	2,074.5	600	150	397.5	93

Table 3(b). Mixture proportions for ASR testing of mortars containing calcined clays (CC or PCC)

Mortar	Moderately reactive (R1) or highly reactive (R2) sand (gr)	Cement (gr)	CC/PCC (gr)	Water (gr)	Flow (%)
Control	1,350	600	0	282	-
10% CC or 10% PCC	1,350	540	60	282	-
15% CC	1,350	510	90	282	-
20% CC or 20% PCC	1,350	480	120	282	-
30% CC	1,350	420	180	282	-
Mortar	Standard sand (gr)	Cement (gr)	CC/PCC (gr)	Water (gr)	WRA (gr)
Control	7,562.5	2,750	0	1,331	0
20% CC	7,562.5	2,200	550	1,331	19.2
20% PCC	7,562.5	2,200	550	1,331	19.8

For drying shrinkage test (ASTM C157-17), four mortar bars (25.4×25.4×285.75 mm) were cast per mixture and moist cured for 24 hours followed by demolding and submerging in a saturated lime bath for 6 days. The initial mass and length were measured at day 7, and the samples were placed in a 50±5% RH, 23 °C environmental chamber for drying. The mass and length of each prism were measured according to ASTM C157 for 5 months. In all measurements, a comparator with accuracy of 0.0025 mm and a balance with accuracy of 0.1 g were used.

Given the high SO_3 content in bituminous FBC fly ash, there is a risk of early age expansion as a result of ettringite formation. To test the potential for this deleterious expansion for each of the mortars included in **Table 3a**, four mortar prisms (285×25×25 mm) were prepared and tested in accordance with ASTM C1038-14b. The prisms were demolded after 23 hours of moist curing, initial gauge readings were taken, and they were subsequently placed in a saturated limewater bath at 23 °C. The length change of each prism was measured after 14 days of storage in the lime bath. The measured expansion was compared against ASTM C1157-17 limit of 0.020%.

FBC fly ash mortar samples were also tested for expansion when exposed to a sulfate solution according to ASTM C1012-18a. Six mortar prims (285×25×25 mm) and nine cubes (50×50×50 mm) were cast and stored over water in a tightly secured container at 35 °C. After 24 hours, the samples were demolded and cured in limewater until reaching a cube compressive strength of 20 MPa. Once the required strength was obtained, initial comparator readings were taken from the prisms, and they were stored in a 50 g/L Na_2SO_4 solution. Prisms were removed from the solution for length measurements at 1, 2, 3, 4, 8, 13, 16, and 24 weeks, after which the solution was exchanged to maintain a pH level of 7±1. The volume expansion at 6 months was compared with the optional physical requirements set by ASTM C618-19 Procedure A.

Finally, the performance and efficiency of these pozzolans in mitigating the alkali-silica reaction (ASR) was evaluated according to ASTM C1567-13. A moderately reactive and a highly reactive aggregate (Class R1 and R2, respectively, per ASTM C1778-16) were used in these tests. The control mixture was prepared with 100% portland cement and several test mixtures were prepared with 10% to 40% replacement of portland cement with each pozzolans. A constant w/cm=0.47 was used in these mixtures and the mass and length change of each mortar bar was measured as a function of time when submerged under a 1M NaOH bath at 80 °C. Mass and length measurements were performed with the accuracy of 0.01 g and 0.0025 mm, respectively. Four replicate prisms were measured per mixture.

In addition to the mortar tests described above, concrete mixtures were designed according to the ACI 211-1 method for formed pavement applications in Pennsylvania. The concrete was designed to be exposed to very severe freezing and thawing and in continuous contact with moisture and exposed to deicing chemicals. Moderate sulfate exposure was considered per ACI 318-19. Also, the Pennsylvania Department of Transportation's (PennDOT's) governing specification requirements for pavement concrete (Class AA) was followed, including limiting the cement content in the range of 348.5 to 446.1 kg/m³, coarse aggregate volume fraction of 36.8 to 48.5%, maximum w/cm = 0.47, and minimum 28-day compressive strength of 25.9 MPa.

Proportions for concrete mixtures containing FBC fly ash are provided in **Table 4**. These had a w/cm = 0.47 and were prepared using an ASTM C150 type I/II portland cement, natural glacial sand from Northumberland, PA (having SSD specific gravity of 2.62, absorption capacity of 1.66%, and fineness modulus of 2.94), and ASTM C33 #57 crushed limestone from Union Furnace, PA (having a nominal size of 25.0 to 4.75 mm, SSD specific gravity of 2.70, absorption capacity of 0.44%, and dry rodded unit weight of 1476.4 kg/m³). In the test mixtures, 20% by mass of the portland cement was replaced with either the anthracite (Ant.1) or the bituminous (Bit.1) FBC fly ash. Sufficient dosages of an air-entraining admixture (AEA MasterAir AE90 by BASF) and WRA were added to obtain a slump of 10±2.5 cm and plastic state air content of 6.0±1.0%. It

was observed that mixtures containing FBC fly ash needed WRA to achieve the target slump and air content.

Table 4. Proportions for the concrete mixtures containing FBC fly ash

Mixture	Coarse Agg. (kg/m³)	Sand (kg/m³)	Water (kg/m³)	Cement (kg/m³)	Fly ash (kg/m³)	AEA (kg/m³)	WRA (kg/m³)
Control	1,098	643	170	362	0	0.47	0
20% Ant.1	1,098	639	170	290	72	0.94	1.40
20% Bit.1	1,098	640	170	290	72	0.47	0.88

Proportions for concrete mixtures containing CC or PCC calcined clays are provided in **Table 5**. These mixtures contained an ASTM C150-17 type I/II portland cement, natural sand (with SSD specific gravity of 2.62, absorption capacity of 1.66%, and fineness modulus of 2.94), and #57 natural gravel (SSD specific gravity of 2.61, absorption capacity of 1.32%, dry rodded unit weight of 97.05 kg/m³). In test mixtures, 20% of the portland cement was replaced with each SCM. The dosages of AEA and WRA were adjusted in order to achieve the target plastic air content of 6.0±1.0% and target slump of 10.2±2.5 cm. Similar AEA and WRA brands were used as the above.

Table 5. Proportions for the control, 20% CC, and 20% PCC mixtures

Mixture	Coarse Agg. (kg/m³)	Sand (kg/m³)	Water (kg/m³)	Cement (kg/m³)	CC/PCC (kg/m³)	AEA (kg/m³)	WRA (kg/m³)
Control	1,098	643	164	349	0	0.46	0.35
20% CC	1,098	634	164	279	70	0.46	1.76
20% PCC	1,098	630	164	279	70	0.46	2.45

The performance of each pozzolan in the above concrete mixtures was evaluated by measuring the concretes' fresh, hardened, and durability properties. These included slump (ASTM C143-15a), plastic state air content (ASTM C231-17a), compressive strength (ASTM C39-18), air-void system parameters in hardened concrete (ASTM C457-16), rapid chloride ion penetration (ASTM C1202-18), and water sorptivity (ASTM C1585-13). For each concrete mixture, 12 cylinders (diameter of 100 mm and height of 200 mm) were cast and moist cured at 23 °C and 100% RH. These were used for compressive strength testing at 7, 28, and 56 days of age, rapid chloride penetrability (RCPT) at 56 days, water sorptivity at 74 days, and air void analysis of hardened concrete at 28 days.

After 28 days of hydration, three 100×120×10 mm sections were cut from each concrete cylinder (perpendicular to the finished surface) and lapped using 75, 35, 17.5 and 12.5 μm grit sizes (No. 220, 320, 600, and 800, respectively). Black marker and $BaSO_4$ powder were used to enhance surface contrast, resulting in a black surface with white air voids. The RapidAir 457 automated imaging system was used to analyze the air void distribution within the hardened concrete (ASTM

C457-16). The volume fraction of air voids (vol%), their spacing factor (mm), and specific surface (mm^{-1}) were determined in the hardened concrete. This analysis was conducted on three samples per concrete mixture.

The rapid chloride penetrability test (RCPT) was used to monitor the quantity of electrical charge passed through 50-mm-thick concrete slices during a 6-hour period. For this purpose, three disk samples (diameter of 100 mm and height of 50 mm) were cut from each 56-day concrete cylinder, coated on the sides with epoxy, and vacuum-saturated according to the procedure described in ASTM C1202-18. During testing, a potential difference of 60 V was maintained across the two ends of the disks, one side in contact with 3% NaCl and the other with a 0.3 N NaOH solution. The total charge passed in coulombs was measured as an indicator of the sample resistance to chloride ion penetration.

Similarly, three disk samples (diameter of 100 mm and height of 50 mm) were cut from each 56-day concrete cylinder and used to measure the rate of water absorption by capillary suction (ASTM C1585-13). Prior to testing, the samples were vacuum-saturated, maintained at 50 °C and 80% RH for 3 days, and subsequently stored in separate sealable containers at 23 °C for 15 days. All surfaces except that exposed to water were sealed and the samples were placed over water (water level was 1-3 mm above the bottom of the sample), to measure the mass gain after 1, 5, 10, 20, 30, and 60 min and at specified intervals up to 7 days.

The results of the above pozzolan characterization and concrete performance testing are included in the next chapter.

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CHAPTER 3

Findings

In this chapter, the results of physical and chemical properties of the anthracite and bituminous fly ashes as well as the impure and purified calcined clay are presented. The physical properties were performed on all four fly ashes. Then, one source of anthracite (Ant.1) and one source of bituminous (Bit.1) were taken for more extensive characterization (i.e., XRF, SEM, and XRD analysis). Furthermore, the performance of Ant.1, Bit.1, and impure (CC) and purified calcined clay (PCC) in mortar and concrete tests are reported.

PERFORMANCE OF FBC FLY ASHES

Physical Properties

The physical properties of the four FBC fly ashes are shown in **Table 6**. These generally satisfy ASTM C618-19 requirements. Although the fineness of both anthracite fly ashes in the as-received form was greater than the maximum allowable limit of 34%, when Ant.1 and Ant.2 fly ashes were passed through #140 (105 µm) and #100 sieves (149 µm), respectively, they complied with the ASTM fineness limit. These sieved anthracite fly ashes were used in the remaining tests reported here. The bituminous FBC fly ashes were tested as received.

Table 6. Physical properties of four fly ashes

Test	Ant.1	Ant.2	Bit.1	Bit.2	ASTM C618 limit
Moisture content (%)	0.31	0.12	0.32	0.37	3.0
Fineness (%)	26*	32**	28	26	34
Water requirement (%)	109.0	103.3	108.9	106.9	115
7-day SAI (%)	103.6	86.0	85.0	104.1	75
28-day SAI (%)	99.2	80.7	91.2	112.6	75

*Fineness of the Ant.1 passing #140 sieve is reported.
**Fineness of the Ant.2 passing #100 sieve is reported.

The water requirement of the FBC fly ashes, except for Ant.2, was observed to be larger than the ASTM C618 limit for conventional PC fly ash (105%). This is justifiable given the angular particle shape of FBC fly ash resulting from a low combustion temperature (<900 ºC) [15]. The 105% limit

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in ASTM C618 was developed based on the spherical particle shape of conventional fly ash, which improves concrete workability as a result of a ball-bearing action. On the other hand, FBC fly ash particles are angular and it makes sense to compare their water requirement with the limit of 115% maximum established in ASTM C618 for class N, natural pozzolans. In this case, the measured water requirement of FBC fly ashes meets that ASTM C618 limit.

The strength activity index (SAI) of the fly ashes were measured according to ASTM C311 at 7 and 28 days to quantify a measure of the pozzolanic reactivity of each fly ash. The results are shown in **Table 6**, showing that all fly ashes meet the ASTM C618 minimum requirement of 75%. The results suggest that Ant.1 and Bit.2 fly ashes are more reactive among the four tested. In particular, Bit.2 fly ash shows the highest reactivity, outperforming the strength of a control portland cement mixture by 12% at 28 days.

For the remaining physical properties, only Ant.1 and Bit.1 fly ashes were tested (see **Table 7**). Laser diffraction testing showed that both Ant.1 and Bit.1 have a similar particle size distribution with a median particle size (D50) that is close to that of conventional PC fly ash (20-30 μm) [49]. The soundness results suggest that the tested fly ashes don't pose a risk of deleterious expansion caused by the hydration of free CaO and/or MgO.

Table 7. Particle size distribution and soundness for Ant.1 and Bit.1

Test		Ant.1	Bit.1	ASTM C618 limit
Particle size distribution	D10 (μm)	2.95	3.42	--
Particle size distribution	D50 (μm)	28.7	26.1	--
Particle size distribution	D90 (μm)	128.0	102.5	--
Soundness (%)		-0.02	-0.03	±0.8

Chemical and Mineralogical Properties

The XRF analysis for both Ant.1 and Bit.1 fly ashes can be seen in **Table 8**. The bulk chemistry of the portland cement is also included. The sum of oxides $SiO_2 + Al_2O_3 + Fe_2O_3$ for both fly ashes is larger than 50%, satisfying ASTM C618 requirements. Both fly ashes have CaO<18% and can be classified as equivalent to class F fly ash. However, Ant.1 fly ash has a significantly lower CaO content in comparison with Bit.1 fly ash. It should be noted that a large portion of the CaO in Bit.1 fly ash is associated with the mineral anhydrite ($CaSO_4$) that is present as a result of flue gas desulfurization in this fly ash.

Both fly ashes show $Na_2Oeq<4.0$, suggesting that they may be suitable for mitigating ASR according to ASTM C1778. The ASR mitigation effectiveness results for these fly ashes are reported later in this chapter. To ensure volumetric stability, and in addition to the soundness criteria reported earlier, ASTM C618 limits the SO_3 content of fly ash to 5.0%. While the Ant.1 meets this criterion, Bit.1 has higher sulfur content (9.83%). This may result in a deleterious expansion due to ettringite formation. An elevated sulfur content in Bit.1 fly ash is in agreement with the high sulfur content of the bituminous coal. The potential for volumetric expansion was tested according to ASTM C1038 and the results will be presented later in this chapter.

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Table 8. Chemical composition of FBC fly ashes

Oxide (wt%)	Portland cement	Ant.1	Bit.1	ASTM C618 limit
SiO_2	19.41	50.10	37.64	--
Al_2O_3	4.61	22.54	16.88	--
Fe_2O_3	3.82	7.66	9.91	--
$SiO_2+Al_2O_3+Fe_2O_3$	27.84	80.30	64.43	$\geq$50.0% for fly ash (C or F); $\geq$70.0% for natural pozz. (N)
CaO	60.78	5.06	15.39	$\leq$18.0% (Class F fly ash); >18.0% (Class C fly ash); Report only (Class N)
SO_3	4.00	2.39	9.83	$\leq$5.0% for fly ash (C or F); $\leq$4.0% for natural pozz. (N)
K_2O	n/a	2.90	2.09	--
Na_2O	n/a	0.35	0.24	--
Na_2O_{eq}	0.90	2.26	1.62	$\leq$4.0% per ASTM C1778-19b
TiO_2	n/a	1.34	0.91	--
MgO	2.91	0.75	1.29	--
P_2O_5	n/a	0.14	0.13	--
CO_2	1.69	n/a	n/a	--
LOI	2.13	6.65	5.21	$\leq$6.0% for fly ash (C or F); $\leq$10.0% for natural pozz. (N)
Carbon (LECO IR)	--	6.26	3.80	--

Another concern is the high LOI values for fly ashes, which may cause problems for air-entraining concrete. ASTM C618-19 allows a maximum 6.0% LOI for fly ash. LOI values greater than 3% are usually considered to require a higher dosage of air-entraining admixtures (AEA) and may result in inconsistent air entrainment and strength of concrete. To better understand the nature of LOI in fly ashes, LECO IR analysis was performed to measure the total carbon content (organic + inorganic) in each fly ash. In summary, Ant.1 fly ash has a high LOI that exceeds the ASTM C618 limit. This LOI is almost entirely associated with the carbon content of this fly ash. As such, LOI mitigation strategies such as carbon burnout, electrostatic separation, or chemical neutralization should be explored for this fly ash. For Bit.1 fly ash, LOI is elevated but is in compliance with the ASTM C618 limit. Additionally, a considerable portion of the LOI is not associated with the mass percent of carbon present in this fly ash. As such, LOI mitigation measures may not be necessary for this fly ash.

In summary, the FBC fly ashes were found to satisfy ASTM C618 physical and chemical requirements for Class F fly ash, with the following exceptions:
- Their water requirement did not meet the 105% limit for fly ash but met the 115% limit for Class N pozzolan, and this is understandable given the angular particles of FBC ash;
- The SO_3 content for Bit.1 fly ash exceeds the 5.0% limit, and this is associated with the presence of anhydrite in this fly ash; and
- The LOI content for Ant.1 fly ash exceeds the 6.0% limit.

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SEM and XRD Analyses

SEM imaging for Ant.1 and Bit.1 FBC fly ashes (**Figure 6**) shows that contrary to the spherical shape of conventional fly ash, FBC fly ash particles have sub-angular shape and internal porosity, consistent with the lower combustion temperature of CFBC boilers. These result in a higher water requirement as reported earlier and will require a higher dosage of water-reducing admixture in concrete to achieve a target slump value. This was reported in Table 4 in Chapter 2.
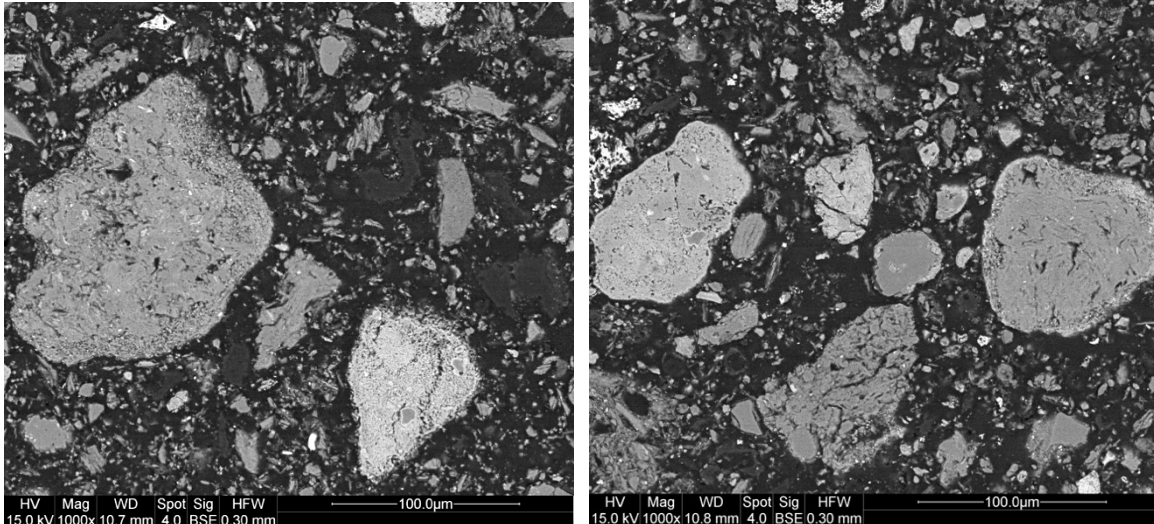
Figure 6. SEM images of Ant.1 (left) and Bit.1 (right) FBC fly ashes

The XRD patterns and Rietveld quantification results for Ant.1 and Bit.1 fly ashes are presented in **Figure 7**. Both fly ashes show amorphous contents close to ~50%; this is smaller than the typical glass content of PC fly ash (>75% [50]). This was anticipated, given the lower combustion temperature of FBC boilers (<900 °C) versus the conventional PC boilers (<1,750 °C). Other reactive phases include anhydrite and free lime. Also, the clay phases (talc and muscovite) are potentially reactive, depending on their degree of calcination. As such, the sum of reactive and potentially reactive phases is 74.5% for Ant.1 fly ash and 78.5% for Bit.1 fly ash. This is more in line with the reactive glass content of PC fly ash. Quartz and hematite phases are non-reactive. Another notable observation is the higher quantity of anhydrite and free lime in the bituminous fly ash, which agrees with its higher CaO and SO$_3$ contents.
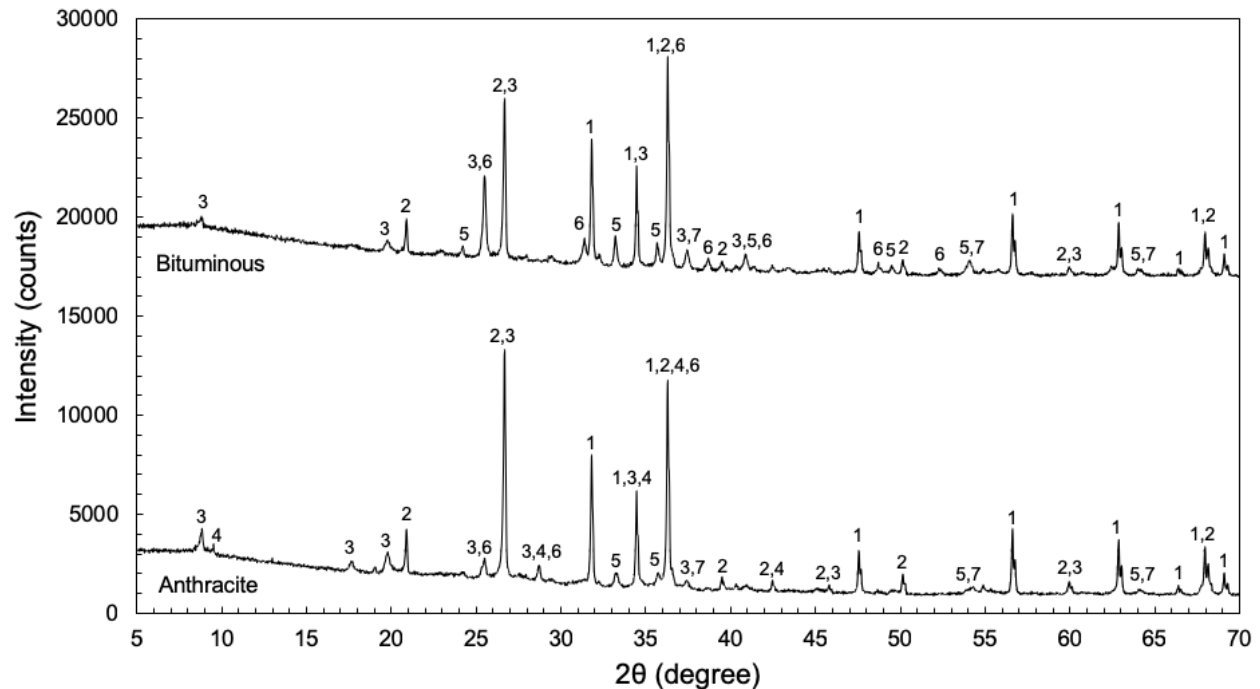
	Anthracite	Bituminous
1 Zincite [ZnO]		
2 Quartz [SiO_2]	22.5%	16.4%
3 Muscovite [$K_{0.8}Na_{0.2}Fe_{0.05}Al_{2.95}Si_{3.1}O_{10}(OH)_2$]	14.5%	15.3%
4 Talc [$Mg_3Si_4O_{10}(OH)_2$]	6.1%	-
5 Hematite [Fe_2O_3]	3.0%	4.3%
6 Anhydrite [$CaSO_4$]	2.9%	11.7%
7 Lime [CaO]	1.0%	2.7%
Amorphous + others	50%	48.8%

Figure 7. Quantitative XRD of Ant.1 and Bit.1 fly ashes

Performance of FBC Fly Ashes in Mortar Tests

The performance of Ant.1 and Bit.1 FBC fly ashes was further evaluated by measuring setting time (ASTM C403-16), and the results are provided in **Table 9**. Replacement of cement with FBC fly ash delayed the time of setting compared to the control mixture. This is likely associated with the slower reactivity of the fly ashes compared to portland cement and is common in concretes containing SCM [51]. Among FBC fly ashes, Bit.1 showed further delays in setting, in agreement with its smaller strength activity index. In addition, the high content of anhydrite (11.7% wt. per QXRD) in bituminous may have affected its setting performance. Similar to gypsum, anhydrite can retard the hydration of C₃A by supplying sulfate ions to the pore solution [52].

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Table 9. Initial and final setting time of concrete

Sample	Initial setting time (min)	Final setting time (min)
Control mixture	355	480
Ant.1	450	620
Bit.1	545	700

To evaluate the impact of the FBC fly ashes on the volume stability of concrete, mortar mixtures were prepared and tested as described in Chapter 2. **Figure 8** shows that drying shrinkage results for mortars containing Ant.1 or Bit.1 fly ashes in comparison with the control mortar. It is observed that mortars containing Bit.1 showed greater drying shrinkage compared to Ant.1 and control samples. The higher rate of shrinkage in bituminous samples during the initial two weeks has mainly contributed to this difference. After the two-week drying period, all samples showed a relatively constant increase in shrinkage with time. The shrinkage of bituminous samples exceeds the control mixture by 0.017%, which is within ASTM C618-19 limits (maximum 0.03%). Meanwhile, the fly ash mortars had a slightly higher drying mass loss compared to the control mixture. This is likely associated with a higher w/cm in the fly ash mortars that was needed to achieve similar workability/flow, as described in **Table 3(a)**.

The potential for early expansion of mortars cured under water was evaluated using the ASTM C1038 test. The average 14-day expansion of four mortar bars per mixture stored in saturated limewater was measured as 0.008%, 0.005%, and 0.024%, for the control, Ant.1, and Bit.1 mixtures, respectively. While the control mixture and the one containing 20% Ant.1 fly ash (whose SO_3 content was less than that of portland cement) showed negligible expansion, the mortar containing the Bit.1 fly ash (having SO_3 content of 9.83%) expanded beyond ASTM C1157's suggested threshold of 0.020% but below 0.04%, which is commonly assumed as the tensile strain capacity of concrete. It is safe to assume that this level of expansion is not deleterious by itself; however, it is advisable to monitor the volume stability of mortar or concrete containing high SO_3 FBC fly ash over a long term and in exposure to moisture, to more confidently rule out the risk of volume instability. Our earlier study [15] on this bituminous FBC fly ash suggested that its anhydrite is highly soluble and results in elevated levels of SO_4 ions in the solution. This can combine with the dissolved alumina and calcium to form ettringite, which is likely responsible for the observed expansion of the bituminous fly ash mortars when cured in limewater.

(a)

(b)
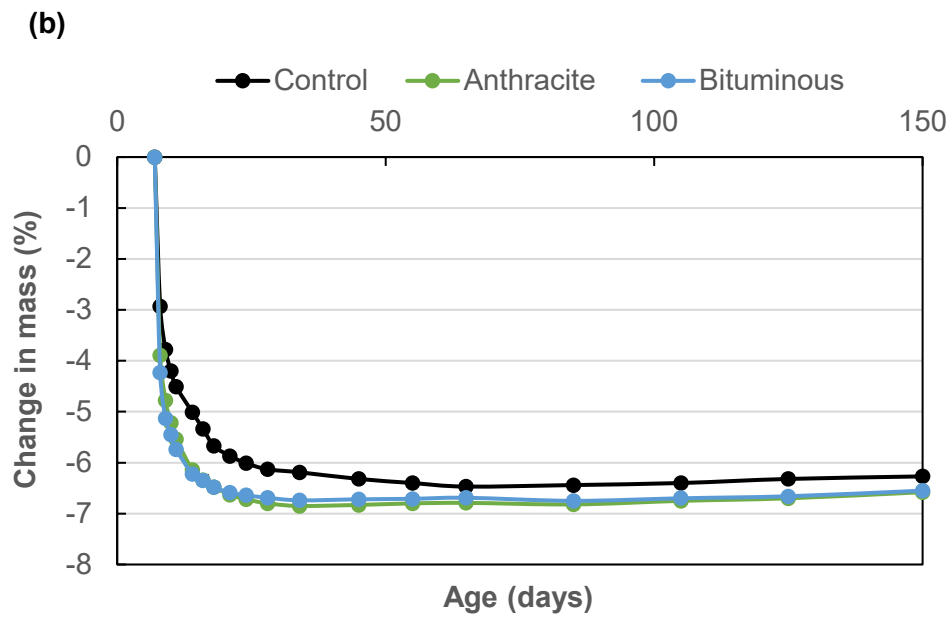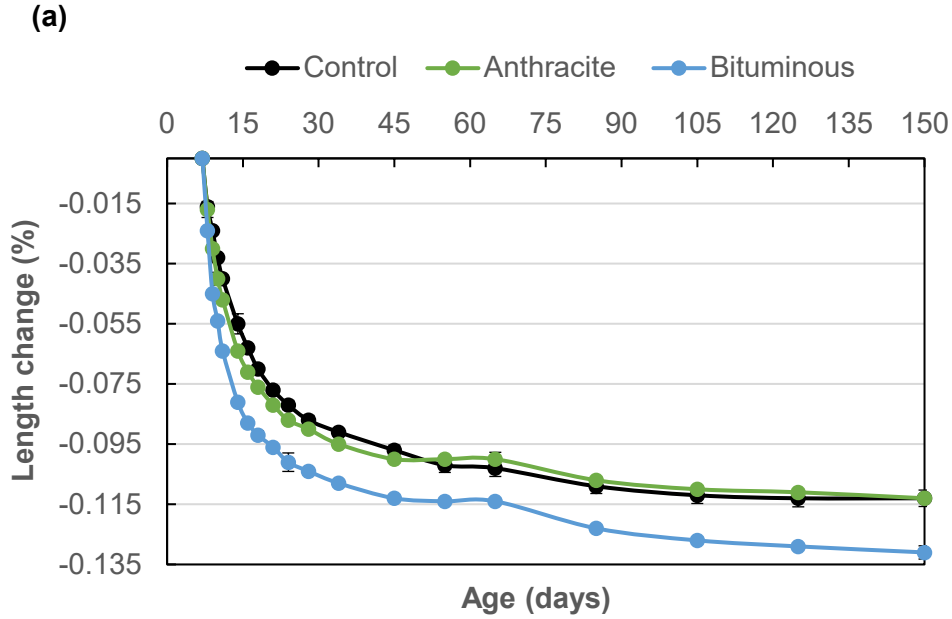
Figure 8. (a) Drying shrinkage and (b) change in mass of mortar samples containing control, 20% Ant.1 and 20% Bit.1

To evaluate the potential for deleterious expansion as a result of external sulfate attack, mortar mixtures were prepared and tested according to ASTM C1012. The mixture proportions for these mortars were provided earlier in **Table 3(a)**. **Figure 9** shows the average expansion of six mortar bars per mixture as a function of time when stored in a 50 g/L (0.35 mol/lit) Na_2SO_4 solution. The control and the Ant.1 fly ash mortars met ASTM C618's optional expansion limit of 0.10% at 6 months for moderate sulfate exposure applications. Even ASTM's limit of 0.05% at 6 months for severe sulfate exposure applications was met. However, the mortar containing the Bit.1

fly ash far exceeded these limits. There are several factors that may explain the poor sulfate attack performance of mortar with the bituminous fly ash. External sulfate attack is the result of conversion of monosulfate AFm to ettringite according to [53]:

$$(CaO)_4(Al_2O_3)(SO_3)(H_2O)_{12} + 2Ca(OH)_2 + 2SO_4^{2-} + 20H_2O$$
$$\rightarrow (CaO)_6(Al_2O_3)(SO_3)_3(H_2O)_{32} + 4OH^-$$
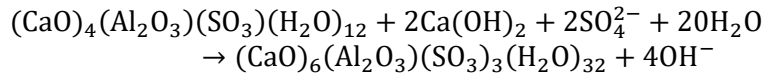
Ettringite formation results in a crystallization pressure that pushes away and opens up microcracks within concrete, resulting in macroscopic damage. As shown by the chemical reaction above, the availability of portlandite is prerequisite for ettringite formation. Fly ashes with low CaO content, such as the anthracite fly ash, are very effective in consuming portlandite via pozzolanic reaction. In contrast, a higher concentration of portlandite is expected in the mixture with the bituminous fly ash due to its higher CaO content and the presence of free lime. This is in agreement with past research on conventional fly ash reporting that concretes containing high-calcium fly ashes are more susceptible to sulfate attack [54,55]. For example, researchers have reported poor performance for mixtures containing class C fly ash, when exposed to sulfate solutions [56,57], while class F fly ash improved the resistance against sulfate attack [58,59].
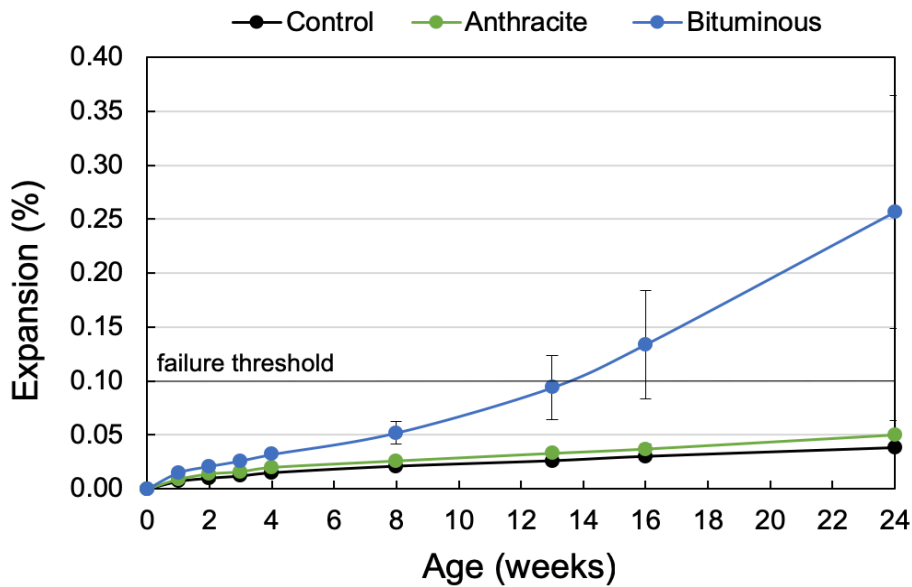
Figure 9. Expansion of mortar samples stored in Na$_2$SO$_4$ solution (ASTM C1012)

Further, gypsum is formed in a reaction between portlandite and sodium sulfate [60-62]. As such, the mixture with the bituminous fly ash is more vulnerable due to increased availability of portlandite. It is worth noting that both Ant.1 and Bit.1 fly ashes contain a significant Al$_2$O$_3$ content, which may contribute to ettringite formation in reaction with portlandite and the available external sulfates. It is also possible that the initial expansion of this mortar due to its higher SO$_3$ content, as discussed above in the context of ASTM C1038 results, reduced its residual tensile strain capacity and accelerated the onset of cracking. Once cracked, the penetration of external sulfates and the resulting expansion and deterioration of the mortar prisms are accelerated. It is noted that after 8 weeks of sulfate exposure, the standard deviation of expansion readings for the

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bituminous mortar became significant and visible microcracking was observed in the samples, consistent with acceleration of the measured expansion. Overall, it can be concluded that while the anthracite fly ash can tolerate moderate or even severe sulfate attack, the use of bituminous fly ash should be avoided in concretes exposed to external sulfates. Further research on exploring and mitigating the potential deleterious expansion of FBC fly ashes in exposure to external sulfates is merited. It is important to determine whether the high SO_3 content or the kinetics of Al_2O_3 dissolution, or both are dictating the sulfate resistance of FBC fly ashes. Studying the interactions between the available Al_2O_3 from fly ash and the interground limestone in portland cement and the stability of the resulting carbonate AFm phases will be valuable.

The accelerated mortar bar ASR test (ASTM C1567) results are shown in **Figure 10** using highly reactive aggregate (R2). Replacement of 20% cement with FBC fly ash reduced the 14-day ASR expansion from 0.30% in the control mixture to 0.21% and 0.26% in mortars containing the Ant.1 and Bit.1 fly ashes, respectively. However, these expansions are still above the ASTM failure threshold of 0.1%. The use of 30% Ant.1 and 40% Bit.1 was successful in mitigating the ASR. A higher efficiency of the anthracite fly ash is in agreement with its lower CaO and higher $SiO_2+Al_2O_3$ contents in comparison with the bituminous fly ash.
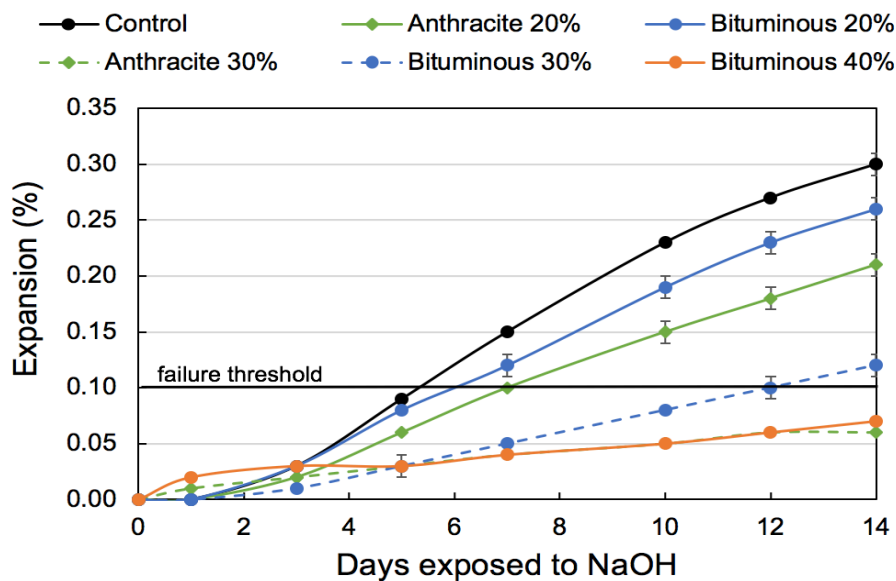
Figure 10. ASR-induced expansion of mortar samples in ASTM C1567 test

Performance of FBC Fly Ashes in Concrete

As discussed earlier in Chapter 2, concrete tests were also performed to evaluate the performance of Ant.1 and Bit.1 fly ashes in concrete. For this purpose, a concrete mixture was designed according to the ACI 211-1 method for formed pavement applications in Pennsylvania. The concrete was designed to be exposed to very severe freezing and thawing and in continuous contact with moisture and exposed to deicing chemicals. Moderate sulfate exposure was considered per ACI 318-19. Also, the Pennsylvania Department of Transportation's governing specification requirements for pavement concrete (Class AA) were followed. **Table 4** presented the mixture

proportions for the control and test mixtures. In the test mixtures, 20% by mass of portland cement was replaced with FBC fly ash.

Table 10 shows the fresh and hardened properties of these concrete mixtures. As discussed earlier, the 20% FBC fly ash test mixtures were prepared by adding sufficient dosages of WRA and AEA (**Table 4**) to achieve a target slump and air content similar to those of the control mixture. These mixtures produced compressive strength values comparable to those of the control (100% cement) mixture at 7, 28, and 56 days of age, despite containing higher air content (~1%) in the fly ash mixtures (see **Figure 11**). The hardened air spacing factor for the control and test mixtures was less than 0.200 mm, which is the maximum allowable limit specified by ASTM C457-16 to provide acceptable freeze-thaw durability. Both fly ash concretes showed a smaller spacing factor than the control, and this is advantageous.

Table 10. Effect of FBC fly ash on the properties of concrete

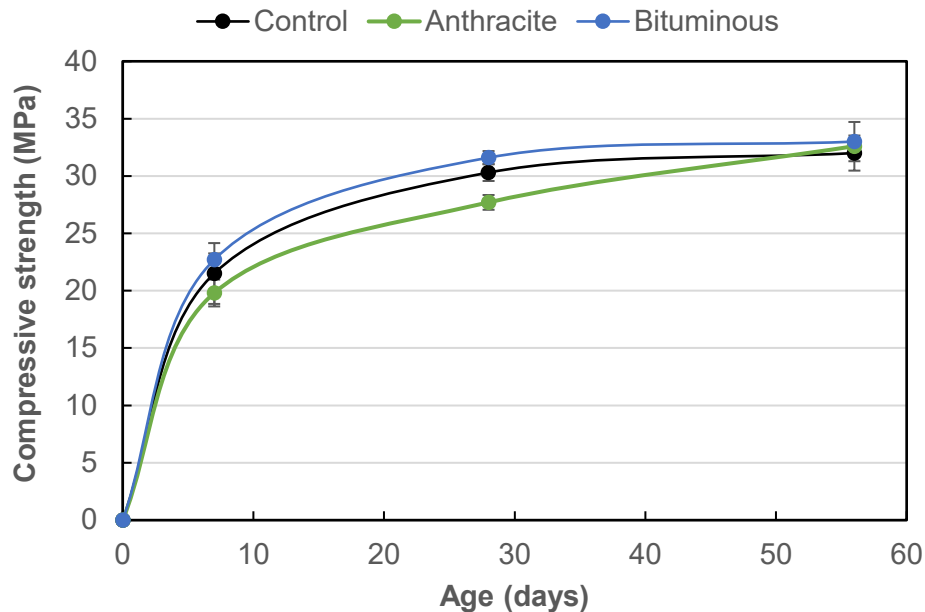| Properties	Control	Ant.1	Bit.1
Slump (mm)	83	127	114
Fresh air content (vol %)	6.0	6.8	6.8
Hardened air content (vol %)	7.1	8.0	8.1
Air-void spacing factor (mm)	0.170	0.120	0.120
Air-void specific surface area (mm^{-1})	22.92	27.09	30.23
Chloride ion penetration at 56 days (coulombs)	3,024	1,291	1,679
Initial sorptivity at 56 days (mm/s$^{0.5}$)	15.3	15.8	9.2
Secondary sorptivity at 56 days (mm/s$^{0.5}$)	7.4	9.1	5.8

Figure 11. Compressive strength of concrete cylinders after 7, 28, and 56 days of hydration

The ion penetrability (ASTM C1202) results, displayed in **Table 10**, show a significant reduction in the total amount of charge passed through 56-day concrete samples, by partial substitution of cement with FBC fly ash. Based on ASTM C1202-18, the control samples demonstrate "moderate" chloride ion permeability (2,000–4,000 coulombs), while the FBC fly ash samples are classified with "low" permeability (1,000–2,000 coulombs).

The results for the water sorptivity test (ASTM C1585) in 56-day concrete samples is provided in **Figure 12**. The reported absorption (I) represents the change in mass of each test sample (in grams) divided by the product of the cross-sectional area (mm^2) of the sample and the density of water (0.001 g/mm^3). Each data point represents an average of the measurements performed on three duplicate samples. Absorption follows a linear relationship with the square root of time elapsed, and the constant of proportionality is the rate of water absorption, also known as "sorptivity." According to ASTM C1585, the initial rate of water absorption is the slope of the line that best fits (with a correlation coefficient greater than 0.98) the data from 1 min ($8\sqrt{sec}$) to 6 h ($147\sqrt{sec}$). The secondary rate of water absorption is calculated in a similar manner based on the results of 1 to 7 days (up to $778\sqrt{sec}$). These sorptivity values are provided in **Table 10**. The error bars representative of the initial and secondary absorption portions of the graphs in **Figure 12** were measured by averaging the standard deviation of all data points from 1 min to 6 h and from 1 to 7 days, respectively.

These results show that the initial sorptivity of concrete containing the Ant.1 is similar to that of the control, while the use of the Bit.1 has reduced both the initial and the secondary rate of water absorption into concrete. However, since the standard error for secondary sorptivity is on the same order as the variation among the results, one cannot claim that the secondary sorptivity values among the three mixtures are statistically different. Note that sorptivity is directly related to the pore structure features such as porosity, pore diameter, and pore connectivity. Mercury intrusion porosimetry (MIP) is recommended for further analysis of pore structure.
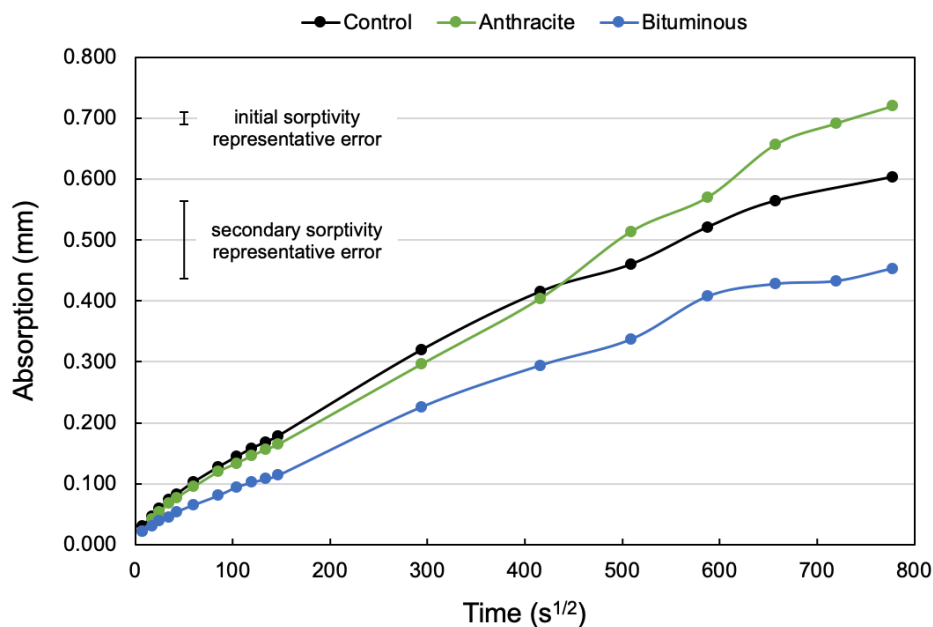

Figure 12. Rate of water absorption in concrete samples measured according to ASTM C1585

PERFORMANCE OF CALCINED CLAYS (CC AND PCC)

SEM

Figure 13 shows the 2D images of SC, CC, and PCC for powders mixed with epoxy. In SC and CC, the solid quartz particles (light grey) are embedded in an agglomeration of the fine groundmass clay particles (darker grey, e.g., kaolinite) and the bright white particles represent iron oxide. After successful purification, the 2D images of PCC powder were taken. It is observed that the quartz particles in PCC are largely absent as compared to SC and CC.

(a) **(c)**
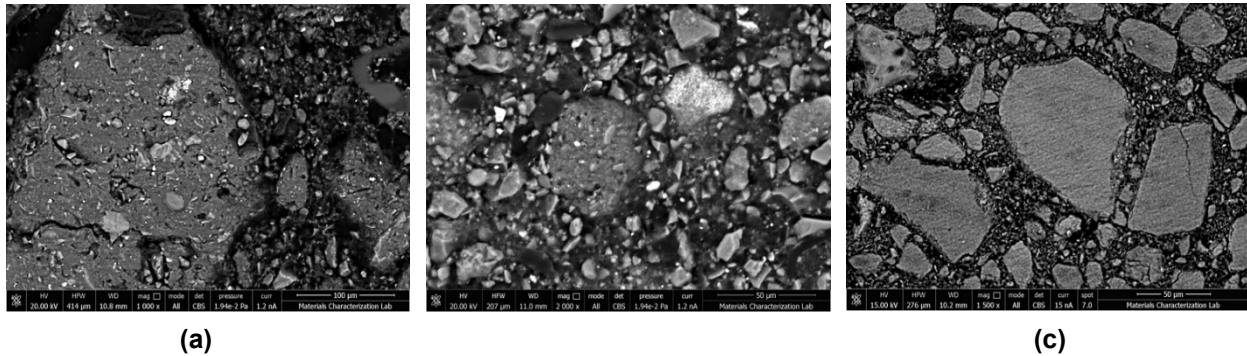
Figure 13. 2D images of (a) SC, (b) CC, and (c) PCC

Physical Properties

The physical properties of CC and PCC could successfully meet the requirements of ASTM C618-19 as shown in **Table 11**. The moisture content of CC and PCC was 0.34% and 0.46%, respectively. Although both CC and PCC samples were calcined at 750 °C, they had slightly regained moisture from the storage environment. The grinding time was chosen such that the samples satisfied the fineness and water requirement limits of ASTM C618. Based on the results for water requirement, it is possible that cement replacement levels greater than 20% may cause workability issues in mortar and concrete samples. Furthermore, the low soundness values measured suggest that the CC and PCC don't pose a risk of deleterious expansion caused by the hydration of free CaO and/or MgO.

The strength activity index of the CC and PCC is also provided in **Table 11**. The 28-day SAI value for CC and PCC mortars is 81.6% and 98.2%, respectively, both of which exceed the 75% minimum limit of ASTM C618. It should be noted that using CC or PCC required higher w/cm in comparison with control mortar having w/cm = 0.484, to meet the ASTM C311 mandate to reach ±5% flow of the control mixture. Since the PCC contained more clay minerals compared to the CC, it needed more water to reach the acceptable flow. Using higher w/cm reduced the SAI of the calcined clay mortar samples. The particle size distribution results for the CC and PCC are presented in **Table 12**. The CC and PCC samples have a median particle size of 8.9 and 20.4 μm, respectively.

Table 11. Physical properties of CC and PCC

Physical properties	Method	CC	PCC	ASTM C618 Limit for Class N pozzolan
Moisture content (%wt)	ASTM C311	0.34%	0.46%	3.0% max.
Density (g/cm^3)	He pycnometry	2.73	2.59	--
Fineness (% >45µm)	ASTM C430	17%	18%	34% max.
Soundness (AC exp. %)	ASTM C151	-0.04%	-0.05%	±0.8% max.
Water requirement (%)	ASTM C311	113.0%	115.0%	115% max.
7-day SAI (S1)	ASTM C311	73.7	81.6	75% min.
28-day SAI (S1)	ASTM C311	89.8	98.2	75% min.
7-day strength, ratio of control (S2)	ASTM C311	87.3	112.4	--
28-day strength, ratio of control (S2)	ASTM C311	105.6	123.6	--

Table 12. Particle size distribution of CC and PCC

Sample	CC	PCC
D10 (µm)	1.46	1.79
D50 (µm)	8.89	20.40
D90 (µm)	44.30	73.10

Chemical and Mineralogical Properties

The results of XRF for portland cement, CC, and PCC are shown in **Table 13**. Based on the results, the chemical composition of the CC and PCC samples met the requirements of ASTM C618-19. The $SiO_2+Al_2O_3+Fe_2O_3$ for the CC and PCC is 96.49% and 92.57%, respectively, which are higher than the 70% minimum limit of ASTM C618. Moreover, the sulfur trioxide (SO_3) for the CC is 0.02% and for PCC is below the detection limit, both of which are lower than the 4.0% maximum. The equivalent SO_3 content from LECO IR testing on the CC and PCC is 0.037% and 0.045%. The Na_2O_{eq} of the CC and PCC is 0.73% and 1.86%, respectively, which is considered low, especially for CC. The comparison between the CC and PCC showed that the SiO_2 content in the PCC significantly decreased after purification due to removal of quartz (SiO_2). It is good to note that the majority of the remaining SiO_2 in the PCC is related to kaolinite, which contains Al_2O_3 and SiO_2 in its structure. The Al_2O_3 content of each calcined clay is a rough and indirect measure of the clay content within CC and PCC. This indicates that PCC contains more clay. As a result of purification, the amount of Na_2O and P_2O_5 in PCC increased, since the deflocculating agent sodium hexametaphosphate remains with clay minerals rather than the separated quartz. This increase in alkalinity of PCC can reduce its efficiency in mitigating ASR, as discussed later.

The LOI of both CC and PCC was 0.42% and 0.79%, respectively. These are very low in comparison with the ASTM C618 limit of 10.0% maximum. The carbon content of the CC and PCC measured by LECO IR was quite low and in agreement with the LOI results.

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Table 13. XRF results for cement, CC, and PCC

Oxide (wt%)	Portland cement	CC	PCC	ASTM C618 limit for Class N pozzolan
SiO_2	19.41	68.49	42.30	--
Al_2O_3	4.61	19.82	35.64	--
Fe_2O_3	3.82	8.18	14.63	--
$SiO_2+Al_2O_3+ Fe_2O_3$	27.84	96.49	92.57	$\geq 70.0\%$
CaO	60.78	0.04	0.08	Report only
SO_3	4.00	0.02	n/a	$\leq 4.0\%$
K_2O	n/a	0.96	1.50	--
Na_2O	n/a	0.10	0.87	--
Na_2O_{eq}	0.90	0.73	1.86	--
TiO_2	n/a	0.83	0.95	--
MgO	2.91	0.24	0.50	--
P_2O_5	n/a	0.12	2.16	--
Cr_2O_3	n/a	0.03	0.06	--
ZrO_2	n/a	0.05	0.04	--
V_2O_5	n/a	n/a	0.06	--
LOI	--	0.42%	0.79%	$\leq 10.0\%$
Carbon (LECO IR)	--	0.122%	<0.08%	--

The QXRD pattern and Rietveld quantification results for SC and CC are summarized in **Figure 14**. The source clay contains 52.6% quartz, 36.2% clay phases (kaolinite, smectite, muscovite), 6.5% hydroxides of iron and aluminum, and the amorphous content is less than 5%. In the CC sample, the quartz content remains nearly the same after calcination, since it is not altered by the heat treatment. The kaolinite, smectite, and the majority of muscovite are altered into noncrystalline dehydroxylated clays (reactive), which make up 42.2% of the sample. Gibbsite and kaolinite start losing the structural water at the temperatures of 300 °C and 600 °C, respectively [41]. The dehydroxylation temperature of muscovite starts at 400 °C and fully disappears at 1,000 °C [63]. Therefore, muscovite did not completely disappear at the calcination temperature of 750 °C. Goethite is calcined to hematite, which is a non-reactive component. The QXRD on PCC is recommended to verify the increase in clay content as well as effectiveness of purification.

	Source clay	Calcined clay
1 Zincite [ZnO]		
2 Quartz [SiO_2]	52.6%	52.4%
3 Kaolinite [$Al_2Si_2O_5(OH)_4$]	26.3%	-
4 Muscovite [$KAl_2(AlSi_3O_{10})(OH)_2$]	7.2%	3.0%
5 Goethite [$FeO(OH)$]	3.4%	
6 Gibbsite [$Al(OH)_3$]	3.1%	-
7 Nontronite [$(CaO)_{0.3}Fe_2Al_4O_{10}(OH)_2$]	2.7%	-
8 Hematite [Fe_2O_3]	-	2.2%
Amorphous + others	4.7%	42.4%
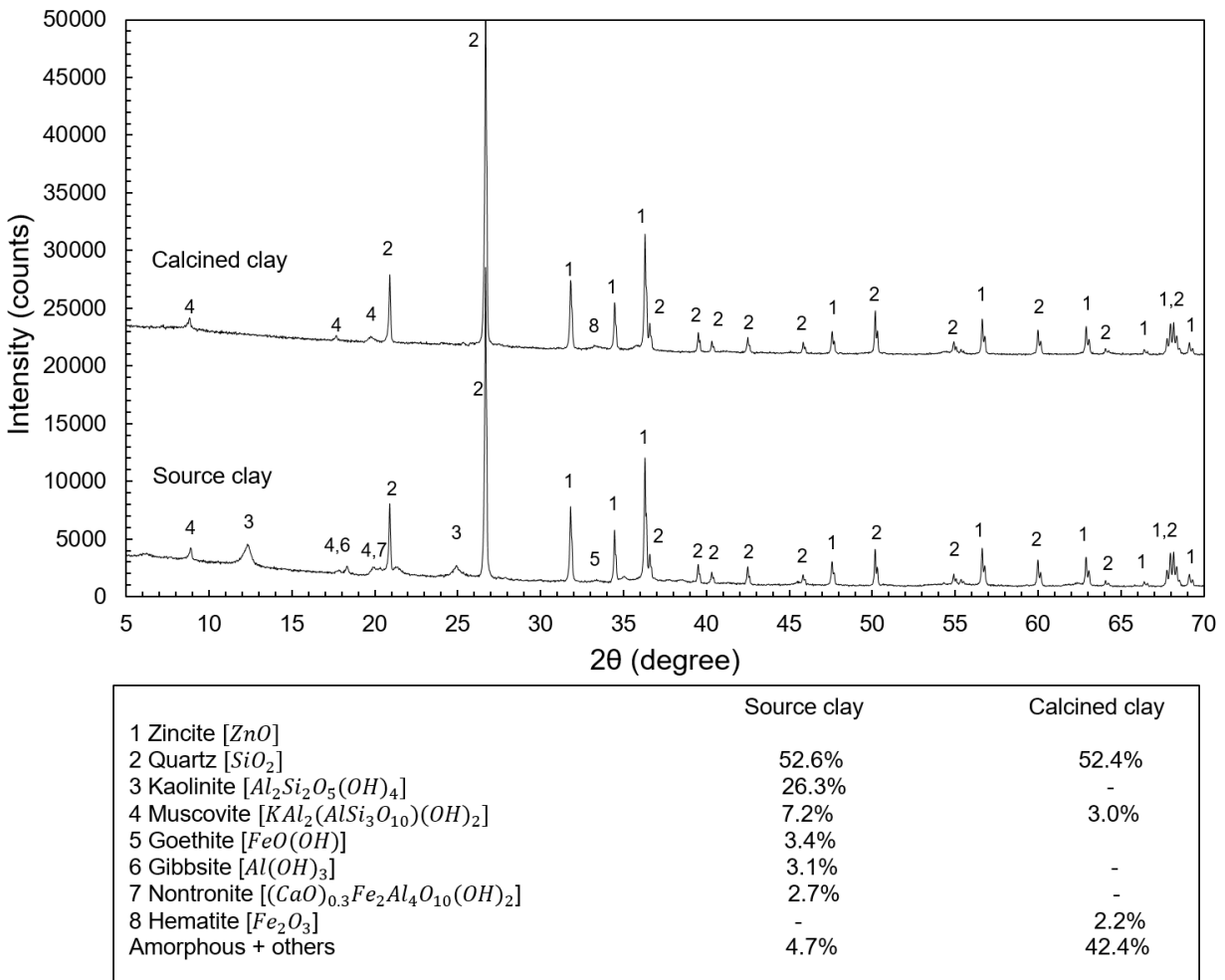
Figure 14. X-ray diffraction patterns and quantitative analysis (wt%) for SC and CC

Performance of Calcined Clays (CC and PCC) in Mortar Tests

Mortar tests were performed to evaluate the performance and impact of calcined clays on time of setting, drying shrinkage, and ASR mitigation efficiency. The mixture proportions for these mortars were provided earlier in **Table 3(b)**. The results of the time of setting are provided in **Figure 15**.

The initial time of setting for the control, 20% CC, and 20% PCC mixtures was 325, 390, and 490 minutes, respectively. The final time of setting for the control, 20% CC, and 20% PCC mixtures was 475, 540, and 680 minutes, respectively. This means that the mortar containing 20% CC and 20% PCC set approximately 1 and 3 hours later than the control mixture, respectively. This is likely associated with the slower reactivity of the calcined clays compared to portland cement and is common in concretes containing SCM [51]. Further, replacement of cement with CC or PCC has increased the demand of WRA, and this may have contributed to the delayed setting. More importantly, the delayed setting observed in the PCC mortars is also caused by the presence of phosphorous (P2O5) in the PCC. Phosphorous compounds have been shown to retard the hydration

of portland cement [64]. In short, using CC and PCC can be considered favorable in warm weather construction when slower setting may be desired. For cold season construction or when rapid setting is desired, using accelerating admixtures in combination with calcined clay should be considered.
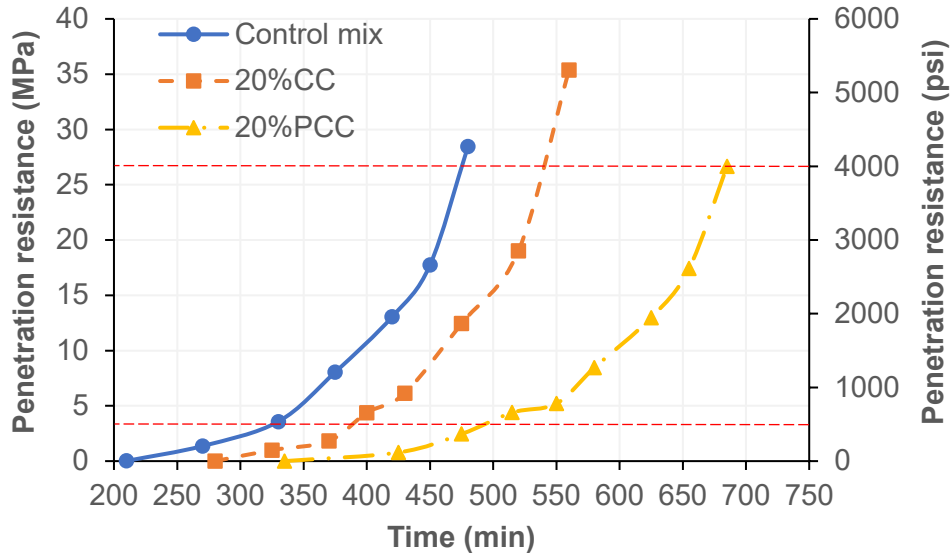
Figure 15. Time of setting results for mortar mixtures

The results of the drying shrinkage and mass loss are provided in **Figure 16**. Both shrinkage and mass change were measured in reference to the length and mass of mortar bars at the end of 7-day moist curing. It is observed that the 20% CC and 20% PCC mixtures shrank faster initially compared to the control portland cement mixture. However, ultimately the 20% CC achieved a similar drying shrinkage as compared to the control mixture, whereas the 20% PCC achieved a lower shrinkage value in comparison with the other two mixtures. Samples containing calcined clay lost more mass, and this was more significant in PCC mortars that contained a higher clay content. Also, it is noted that CC and PCC samples reached a constant mass after about 4 weeks; however, the control mixture equilibrated after 7 weeks. Drying shrinkage did not stop after this moisture content equilibrium, indicating the presence of drying creep. The reasons for the highest mass loss and the lowest drying shrinkage for samples containing PCC may be due to the size and connection of capillary pores. A mercury porosimetry test is recommended for better understanding of the pore size distribution in these systems. It should be noted that all drying shrinkage mortars had the same w/cm = 0.484 (**Table 3(b)**).
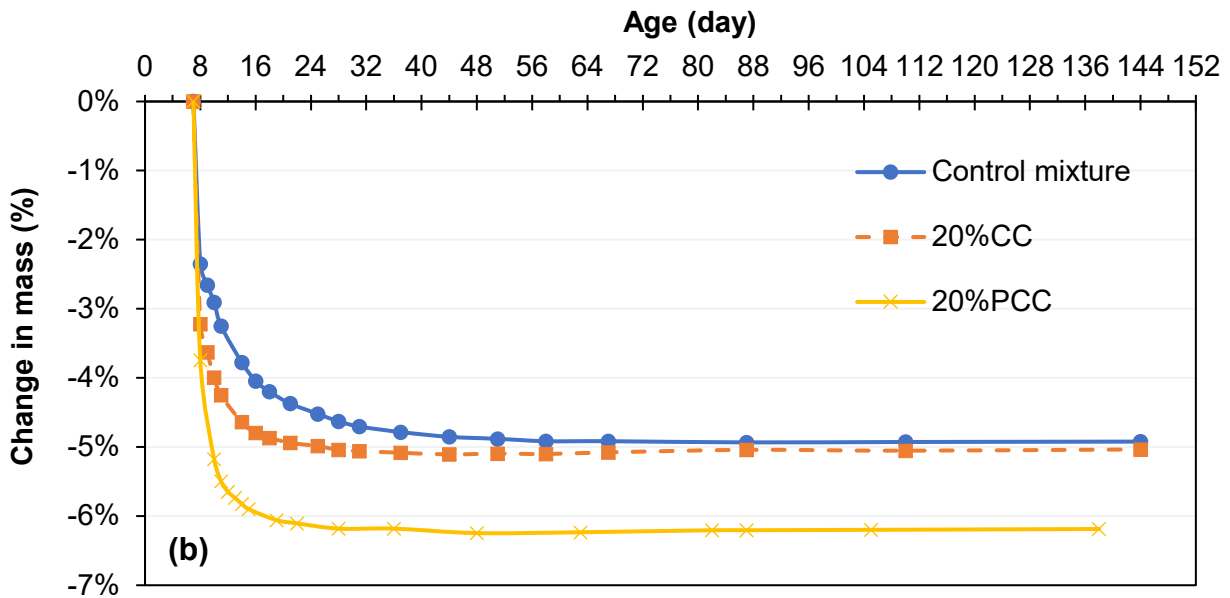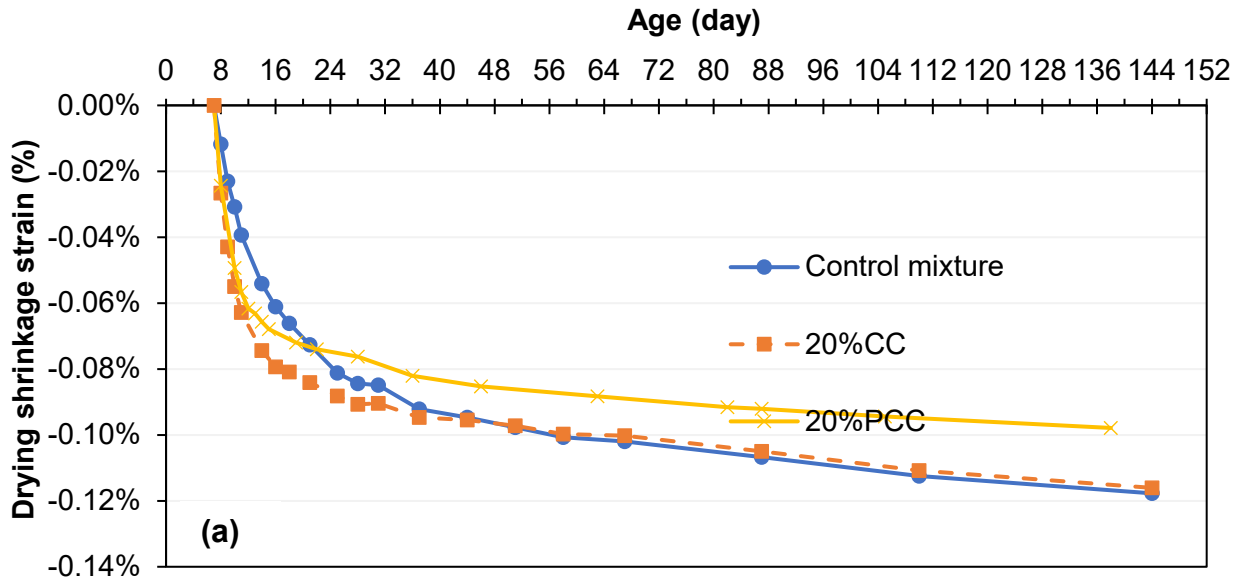
***Figure 16. Drying shrinkage (a) and change in mass (b) versus age during drying
of mortars at 23 °C and 50% RH***

Figure 17 reports the effectiveness of the CC and PCC in mitigating ASR according to ASTM C1567. Mortars containing either a moderately reactive (R1) aggregate or a highly reactive (R2) aggregate were tested. The R1 and R2 designations were based on ASTM C1778 guidelines. It is observed that replacing cement with CC or PCC reduced ASR expansions significantly. For R2 aggregates, replacing 20% cement with CC could improve the expansion of ASR from 0.33% to 0.13% but not below the failure threshold specified by ASTM C1567, which is 0.1% expansion. To completely mitigate ASR using CC for R2 aggregate, 30% replacement was required to reduce the expansion from 0.33% to 0.08%. On the other hand, for the same R2 aggregate, 20% PCC was sufficient to suppress ASR below the failure threshold (from 0.33% to 0.05%). This suggests that

clay purification improves its performance against ASR by removing the inert quartz particles. For the more common moderately reactive (Class R1) aggregates, a lower CC and PCC dosage could mitigate ASR (15% and 10%, respectively). Longer-term ASR testing using the concrete prism test (ASTM C1293) is recommended for future research to more reliably determine the CC and PCC dosage that is required to mitigate ASR for a given reactive aggregate. The expansion of each test mixture versus time can be seen in **Figure 18 (a)** for R2 aggregate and **Figure 18 (b)** for R1 aggregate.

Performance of Calcined Clays (CC and PC) in Concrete

The effects of replacing 20% of cement with CC and PCC on the properties of the pavement-grade concrete mixture are provided in **Table 14**. Mixture proportions for the control and the test mixtures are provided in **Table 5**. All mixtures had a w/cm = 0.47. In the test mixtures, 20% by mass of portland cement was replaced with either CC or PCC.

As shown in **Table 5**, a higher WRA dosage was needed to achieve a target slump of 10±2.5 cm in the 20% CC and 20% PCC mixtures. The fresh density and fresh air content in all three mixtures were similar and were achieved using similar AEA dosages. A hardened air analysis was performed on 28-day moist cured concrete samples using a RapidAir instrument according to ASTM C457-16. The results showed that the hardened air content of the control, 20% CC, and 20% PCC mixtures were 6.3%, 7.1%, and 6.4%, respectively. Furthermore, the spacing factor for all mixtures was 0.151 mm, 0.144 mm, and 0.137 mm, respectively. These values are below the maximum threshold of 0.200 mm, indicating that all mixtures are anticipated to have adequate freeze-thaw durability.
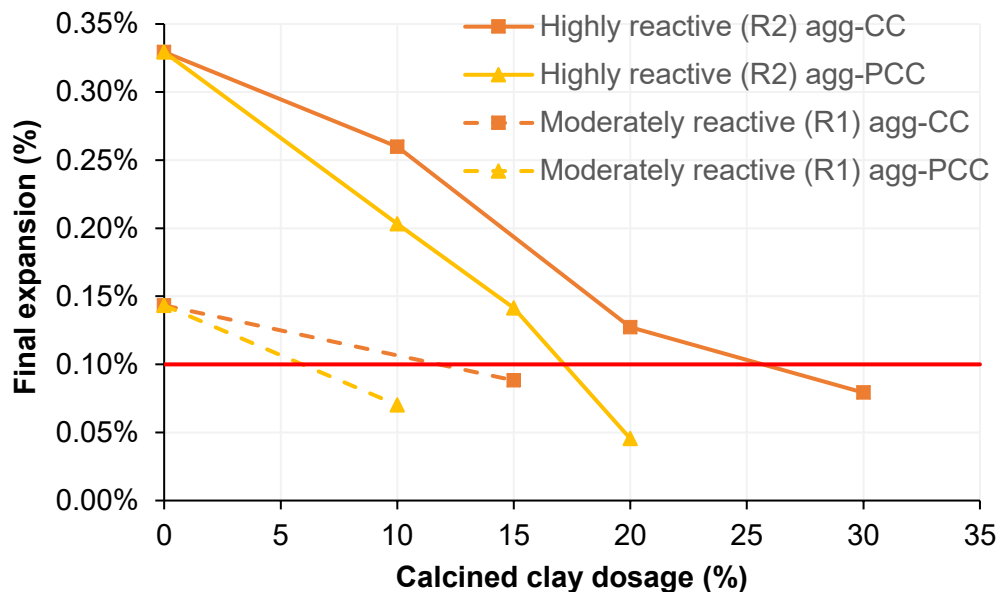
Figure 17. The effectiveness of CC and PCC in mitigating ASR
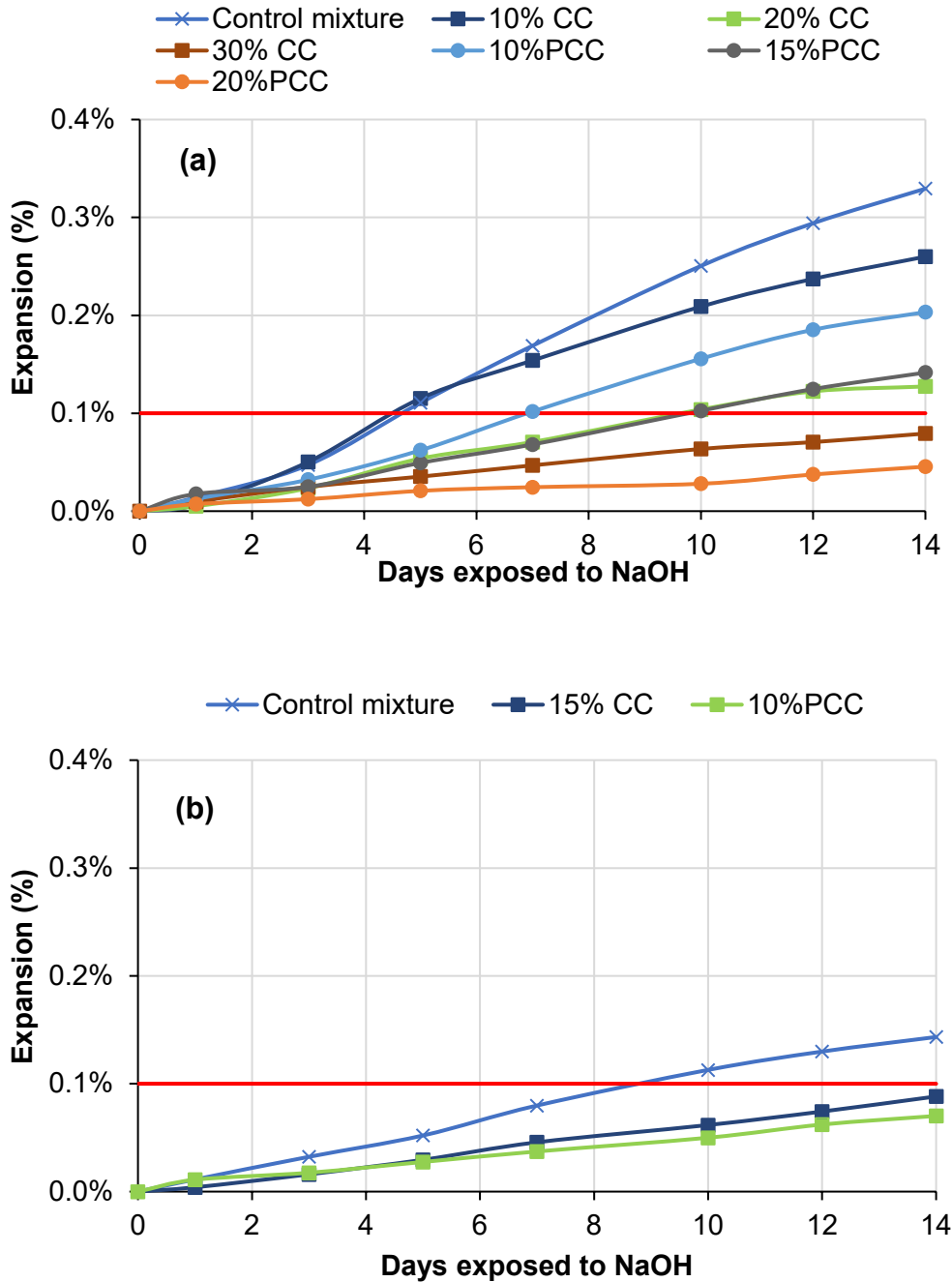
Figure 18. ASR mitigation performance of CC and PCC evaluated by ASTM C1567 test using (a) highly reactive (R2) aggregate and (b) moderately reactive (R1) aggregate

The ion penetrability test (ASTM C1202-18) was performed on the control, 20%CC, and 20%PCC concrete samples after 28 and 56 days of moist curing (**Table 14**). According to the previous study [35], increasing the age at testing reduces the total charge passed through samples during the test. Overall, using PCC showed the best performance among the three mixtures. The 28-day RCPT values indicated that the risk of chloride intrusion into the control concrete was high (>4000

coulombs) and inclusion of 20% CC and 20% PCC reduced the RCPT values by ~20% and ~37%, respectively, which confirmed that the risk of chloride penetration was within the moderate range (2,000–4,000 coulombs). Furthermore, the 56-day results showed that the risk of chloride penetration for all mixtures was within the moderate range; however, replacing 20% of cement with CC and PCC can improve the risk of chloride penetration by 7% and 35%, respectively. This improvement is likely attributable to densification of the pore structure and reduction in the pore solution electrical conductivity as a result of the pozzolanic reactivity of the calcined clay.

Table 14. Impacts of the 20% CC and 20% PCC as cement replacement on the properties of the concrete mixture

Properties	Control mixture	20%CC	20%PCC
Slump (cm)	11.4	12.7	12.7
Fresh density (kg/m³)	2,244	2,214	2,211
Fresh air content (vol %)	6.5	6.8	7.0
Hardened air content (vol %)	6.3	7.1	6.4
Air spacing factor (mm)	0.151	0.144	0.137
RCPT @ 28 days	4,815	3,844	3,042
RCPT @ 56 days	3,752	3,497	2,449
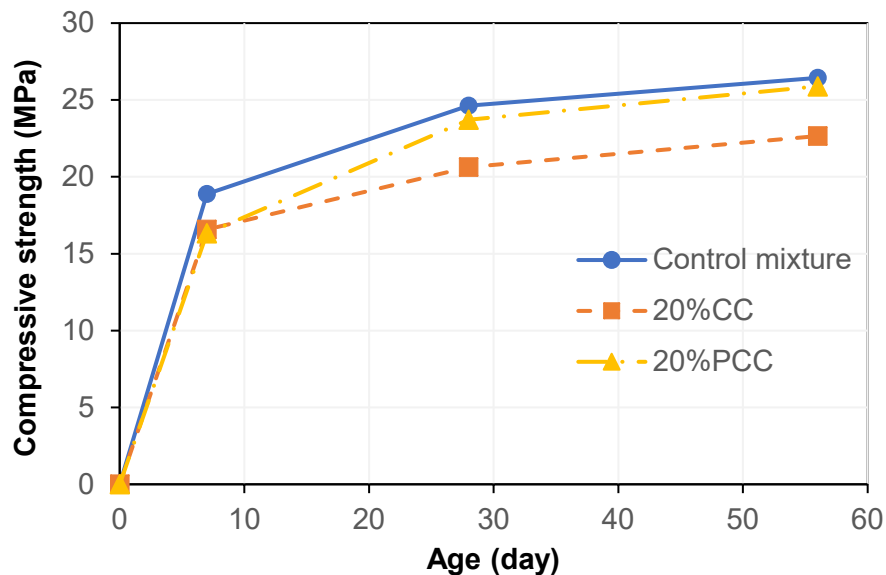
Figure 19. Compressive strength of the control, 20% CC, and 20% PCC concrete mixtures

The results for 7-, 28-, and 56-day compressive strengths of the control, 20% CC, and 20% PCC concrete mixtures are shown in **Figure 19**. The 20% CC mixture showed a lower strength (by ~15%) compared to the control mixture at all ages. The reason for the lower compressive strength of CC may be partially due to the higher hardened air content of the CC mixture and partially due to the impurity of CC (quartz fraction). At 7 days, the control mixture showed the highest strength compared to the other two CC and PCC mixtures, since using calcined clay was

not effective to improve the early-age strength. However, after 28 days, the compressive strength of the 20% PCC increased and became closer to that for the control mixture, and after 56 days the results of the control and the 20% PCC were approximately equal. This means that the reactivity of the PCC started after 7 days of mixing. A reduction in the w/cm of the CC mixture is recommended to improve its compressive strength to above the PennDOT limit of 25.9 MPa (3,750 psi) at 28 days.

COST ANALYSIS

As a final component of this chapter, a preliminary cost analysis was performed and is presented here to assess the economic potential of using FBC fly ash and calcined clay pozzolans in concrete production. The production of pozzolans has been separated into seven main processes: (1) raw materials extraction, (2) required fuel for extraction, (3) beneficiation cost (in this case drying and sieving), (4) calcination (just for calcined clay), (5) grinding and packing, (6) cost of permits and other regulatory requirements, and (7) cost of personnel. The transportation cost is paid by the purchaser.

Cost Analysis for FBC Fly Ash

For FBC fly ash, the major cost is for sieving and grinding to achieve proper median particle size. The energy and cost required to sieve and grind the FBC fly ash is assumed to be similar to the final milling process of portland cement [65]. In this study, LOI mitigation measures are not included.

Cost of sieving and grinding for FBC fly ash = ~ $15/ton

The cost for permits, sampling, testing, characterization, and other QC activities is estimated as 10% of the beneficiation costs.

Cost of permits and testing = 0.1* $15/ton = ~ $1.50/ton

Personnel cost includes salary and benefits for four persons at an annual cost of $90,000 per person divided by the throughput of 100,000 tons/year of fly ash in a given power plant.

Cost of personnel = $3.60/ton

Fly ash transportation cost is assumed to be paid by the purchaser. The total direct cost for producing FBC fly ash is:

Total direct cost = $15 + $1.50 + $3.60 = $20.10/ton

A profit of 20% is considered, resulting in the following price point for FBC fly ash:

Price point = 1.2 * ($20.10) = $24.10/ton

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As a comparison, the cost of conventional pozzolans in the concrete market is in the range of $60 to $130 per ton.

Cost Analysis for Calcined Clay

For excavation and calcination of clay, a $20 million investment was assumed to be required. The total cost includes capital investment, maintenance and operations, fuel, testing, and personnel costs. Capital investment cost is based on the calculated cost of borrowing $20M at an annual interest rate of 5% for a 20-year term and achieving a material throughput of 100,000 tons/year. A clay reservoir of 2,000,000 tons is assumed. At the end of the 20-year operation, the residual/salvage value of the calcination plant is estimated at $5.0M.

Annual loan payment = 12 * $99,000 = $1,188,000
Annual loan per ton of calcined clay produced = $1,188,000/100,000 = $11.90/ton

The maintenance and operations cost is assumed as 10% of the installation cost = $1.20/ton

The cost for permits, sampling, testing, characterization, and other QC activities is estimated as 10% of the calcination cost = 0.1 * (11.90+1.20) = $1.30/ton

It is assumed that the same fuel as used in the production of clinker will be used in the calcination of clay. The energy and cost of calcination of clay has been evaluated to be ~50% of the energy and cost of the production of clinker [65,66]. This means that the fuel cost for calcination of clay is ~$17 per ton.

Personnel cost includes salary and benefits for 12 persons at an annual cost of $90,000 per person divided by the throughput of 100,000 tons/year of fly ash in a given power plant.

Cost of personnel = $10.80/ton

Fly ash transportation cost is assumed to be paid by the purchaser. The total direct cost for calcined clay is:

Total direct cost = $11.90 + $1.20 + $1.30 + $17 + $10.80 = $42.20/ton

A profit of 20% is considered, resulting in the following price point for calcined clay:

Price point = 1.2 * ($42.20) = $50.60/ton

As a comparison, the cost of conventional pozzolans in the concrete market is in the range of $60 to $130 per ton.

CHAPTER 4

Conclusions

As the supply of conventional pozzolans falls further behind the concrete industry's demand, interest in nontraditional pozzolanic materials continues to grow. Impure calcined clays and fluidized bed combustion fly ashes are two promising nonconventional pozzolans. Impure clay sources are abundant in the Eastern and Southeastern United States and also present across central and western areas of the country. Fluidized bed ash has an annual U.S. production of 15 million tons and is specifically prevalent in the Mid-Atlantic region. In this study, four FBC fly ashes with various compositions, one impure calcined clay, and one purified calcined clay were evaluated for their compliance with ASTM C618-19 and AASHTO M 295 specifications and their performance and impact on the fresh and hardened properties of concrete.

CONCLUSIONS RELATED TO FBC FLY ASH

The following conclusions can be drawn for FBC fly ashes. It is noted that four fly ashes were evaluated for their physical properties but only two of the fly ashes were evaluated in the remaining experiments:

- FBC fly ash results from burning coal at 750 ºC to 900 ºC. This lower combustion temperature, in comparison with conventional PC boilers, results in an FBC fly ash with similar chemistry but different mineralogy than the conventional PC fly ash. In addition, FBC fly ash particles are subangular in shape and contain internal porosity, as they don't melt during the combustion process.

- The FBC fly ashes evaluated in this study were found to satisfy ASTM C618 physical and chemical requirements for Class F fly ash, with the following exceptions:
    - The water requirement of 3 of the 4 fly ashes exceeded ASTM's 105% limit set for conventional fly ash but was below the 115% limit for Class N pozzolan. This is understandable given the angular particle shape and internal porosity of FBC fly ash, which stem from its low combustion temperature (<900 ºC);
    - The SO_3 content for Bit.1 fly ash exceeded the ASTM's 5.0% limit, and this is associated with the presence of anhydrite in this fly ash; and
    - The LOI content for Ant.1 fly ash exceeded the ASTM's 6.0% limit, and this is associated with the presence of unburned carbon in this fly ash.

- According to the X-ray diffraction results, the two anthracite and bituminous FBC fly ashes studied contained reactive phases (thermally altered clays, anhydrite, free lime) and inert phases (quartz and hematite). The reactive phases made up 74.5% and 78.5% of the mass

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of the fly ashes. The presence of anhydrite is a notable difference with conventional fly ashes and is a result of internal SO_x scrubbing in FBC boilers via injection of pulverized limestone.

- Concrete mixtures containing 20% FBC fly ash and with proper dosing of water-reducing and air-entraining admixtures could achieve desirable slump, plastic, and hardened state air contents, and air-void spacing factor.

- These concrete mixtures produced a similar compressive strength to that of the control mixture as early as 7 days of age, despite having a slightly higher (~1%) air content. The anthracite fly ash showed a potential for further strength improvement at later ages.

- Replacement of cement with FBC fly ash delayed the setting time. Between the fly ashes, the bituminous fly ash showed further delays in setting, in agreement with its smaller strength activity index and higher anhydrite content, which can retard the hydration of C_3A.

- Using FBC fly ash improved concretes' resistance to chloride ion penetration measured via ASTM C1202 method. The control samples demonstrated "moderate" chloride ion permeability (2,000–4,000 coulombs), while FBC fly ash samples are classified with "low" permeability (1,000–2,000 coulombs).

- The mortar containing the bituminous fly ash exhibited an early-age expansion when cured under limewater. This is likely attributed to formation of ettringite as a result of elevated SO_3 content of this fly ash. Further, this mortar showed poor resistance to external sulfates, which is likely attributable to an increased availability of portlandite due to the higher CaO content of the bituminous fly ash. On the contrary, the anthracite fly ash showed desirable early-age volume stability and long-term sulfate resistance despite having a high Al_2O_3 content.

- Both anthracite and bituminous fly ashes showed acceptable performance with respect to drying shrinkage of mortar bars, meeting the relevant ASTM C618 limit.

- Both anthracite and bituminous fly ashes could mitigate ASR according to the ASTM C1567 test of a highly reactive (class R2) aggregate. The anthracite fly ash was more effective, requiring 30% cement substitution in comparison with the bituminous fly ash that required a dosage of 40% by mass of cementitious materials to mitigate ASR. This was due to lower CaO and higher Al_2O_3 and SiO_2 contents in the anthracite fly ash.

CONCLUSIONS RELATED TO CALCINED CLAY

The following conclusions can be drawn for the impure (CC) and purified (PCC) calcined clays:

- Calcined clay is obtained from calcination of impure kaolinite clay at temperatures around 700 °C. These clays may include several clay minerals (kaolinite, illite, mica, chlorite) and are often intermixed with other minerals such as quartz, feldspar, or calcite.

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- The clay investigated in this study was primarily composed of kaolinite and quartz. It was calcined at 750 °C for 3 hours. It was studied as is (in the impure form). Additionally, a purification process was employed to separate the quartz and increase the kaolinite content, and the properties and performance of this purified clay were also studied.

- For purifying the clay, sedimentation was assisted by the use of 0.5% sodium hexametaphosphate (SHMP) deflocculating agent, which was found successful in separating the source clay into quartz-rich and clay-rich fractions. The possible technical challenges with impure clays (containing considerable amounts of inert fillers and non-reactive phases) and the purification techniques that can be employed to mitigate these problems were discussed. Most commonly, impure clays must be dried, calcined, and milled to a proper particle size. Some impure clays may require more extensive purification to remove the inert materials, while others may be usable as is.

- Both the impure (CC) and the purified calcined clays (PCC) produced and tested in this study met all the mandatory chemical and physical requirements of ASTM C618 for natural pozzolans.

- Concrete mixtures containing 20% CC or PCC using proper dosage of water-reducing and air-entraining admixtures could achieve desirable slump, plastic, and hardened state air contents, and air-void spacing factor.

- 20%CC had 7-, 28-, and 56-day compressive strength values that were ~15% lower than a control mixture with 100% portland cement. However, the compressive strength of 20%PCC samples was similar to that of the control at 28 and 56 days.

- For CC and PCC mortar mixtures, there were 1 and 3 hours' delay in time of setting compared to the control mixture, respectively; this is partially due to the nature of calcined clays and partially due to the high dosage of WRA used in the test mixtures. Additionally, the presence of phosphate in the PCC contributed to delayed setting.

- The studied CC and PCC were proven effective in mitigating ASR. For highly reactive (R2) aggregate, replacing 30% of the cement with CC or 20% of the cement with PCC could mitigate ASR. For moderately reactive (R1) aggregate, 15%CC and 10%PCC was sufficient to suppress ASR.

- Concrete containing 20% CC or 20% PCC reduced the penetration of chloride ion into the concrete by 10% and 35%, respectively, compared to the control mixture. PCC mixture had the best performance in terms of durability against chloride ion penetration.

- In comparison with the control mixture, CC revealed similar drying shrinkage performance; however, PCC shrank less than the control mixture.

SUGGESTED MODIFICATIONS TO RELEVANT SPECIFICATIONS

Calcined clays are already included in ASTM C618 and AASHTO M 295 as a Class N pozzolan. However, many state DOT specifications do not recognize natural pozzolans as an acceptable SCM simply due to lack of history of using Class N pozzolans in that state. We strongly recommend that state DOTs be proactive and adopt AASHTO M 295 language in their specifications so natural pozzolans, including calcined clays, can be considered for approval as an acceptable SCM for use in concrete to produce high-quality and long-lasting concrete structures. We also recommend changing the water requirement limit within ASTM C618 for Class N pozzolan to "report only."

On the other hand, FBC fly ashes currently do not have a specification to allow their evaluation, screening, and use in concrete. Certainly, this lack of governing specifications is a significant impediment against the use of these pozzolans in concrete. This effort serves as a preliminary study showing that FBC fly ashes could have a promising performance as concrete SCM. As such, we strongly recommend further research on these fly ashes in various concrete mixtures to more confidently evaluate their short-term and long-term performance. Such research should pave the way for inclusion of coal-based FBC fly ashes within ASTM C618 specification, for example as Class FB. This way, FBC fly ashes that meet the physical and chemical requirements of ASTM C618 can be used by themselves or blended with other pozzolans for use in concrete. We also recommend that the water requirement limit for Class FB fly ashes be set at 115% maximum.

TECHNOLOGY TRANSFER

Technology Transfer (T2) efforts in this project include:

- Publication of two peer-reviewed journal papers in the *Transportation Research Record* and the *Construction and Building Materials* journals [67]. A third journal paper is currently in preparation on the subject of purification of calcined clay.

- Presentation of the research findings and outcomes at national and regional conferences including the 2020 Transportation Research Board Annual Meeting, the 4th FHWA Workshop on Emerging Developments Related to Concrete Pavement Durability (2019), CIAMTIS's Transportation Asset and Infrastructure Management (TAIM'20) conference, the 2020 Pennsylvania Concrete Conference, and several other DOT and industry meetings.

- The research team is working closely with a company that owns large impure clay resources in the Mid-Atlantic region to process, test, and produce specification-compliant calcined clay pozzolan for the concrete market. The research team is also in communication with two other impure calcined clay producers in central and western United States to test their products and assist in further market adoption of their pozzolans.

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