EVALUATING THE USE OF FLUIDIZED BED COMBUSTION FLY ASH AS
CONCRETE POZZOLAN

A Dissertation in
Civil Engineering

by
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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

December 2019
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Supplementary cementitious materials (SCM) are a key ingredient of today’s concrete and can vastly improve the durability and sustainability of concrete mixtures. While the demand for fly ash and other suitable pozzolans continues to escalate, the supply of high-quality and economically available fly ash has been shrinking. To maintain and expand the market share of concrete products, it is critical that high-quality, long-lasting and cost-competitive concrete is widely available; this requires a stable and abundant supply of cheap fly ash. Fluidized bed combustion (FBC) fly ash is an alternative source of fly ash that is widely available, but currently not used in concrete. This is due to the lack of guidelines and protocols to evaluate the quality/performance of FBC fly ash and identify necessary beneficiation procedures before it can be incorporated into concrete mixtures. The FBC process is a cheaper and more efficient way of burning waste coal compared to conventional pulverized coal combustion (PCC). In this technology, sulfur-absorbing minerals (e.g., limestones) are added as kiln feed and turbulence is increased, to enable combustion at lower temperatures (750-900°C), which in turn reduces NOx emissions. Although FBC fly ash may be a great SCM source, its performance as concrete pozzolan is not yet well understood, and there is a significant need for research to develop guidelines that distinguish usable sources of FBC ash.

To address these knowledge gaps, the purpose of this research is to evaluate the feasibility, performance, hydration, and beneficiation of FBC fly ash and determine if and how this alternative fly ash can be used as a viable pozzolan for concrete. In this study, circulating fluidized bed combustion (CFBC) fly ashes were collected from two sources in Pennsylvania (products of anthracite and bituminous waste coal combustion) and characterized for their physical properties, unburned carbon content, bulk chemistry, mineralogy, and reactivity. Results were compared against the requirements of ASTM C618-19 and areas of non-compliance were identified. Further, the characteristics of CFBC fly ashes were linked to the fresh and hardened properties of concrete.
and mortar mixtures. The fly ashes were used to substitute 20% of Portland cement in concrete mixtures, and their effect on the slump, fresh air content, hardened air properties, compressive strength, chloride ion permeability, and water absorption rate of concrete was evaluated. Equivalent mortar mixtures were also prepared and tested for their drying shrinkage, autogenous shrinkage, expansion in water, resistance to sulfate attack and alkali-silica reaction. The fly ashes met the chemical and physical requirements of ASTM C618-19, except for elevated LOI (in both fly ashes) and elevated SO₃ (in bituminous fly ash). Despite this, concrete with proper slump, air content, and strength development was produced by adequate dosing of chemical admixtures. The high SO₃ content in bituminous fly ash did not produce deleterious expansion during autogenous shrinkage testing and the value of 14-day expansion in water was close to the ASTM threshold. Use of CFBC fly ash was found to be most effective in mitigating chloride ion penetration and alkali-silica reaction. This was mainly due to the contribution of CFBC fly ash in lowering the alkalinity of the pore solution, increasing its aluminum and silicon ion concentration, as well as refining the pore structure. Both fly ashes did not have a significant effect on drying shrinkage. Samples containing anthracite fly ash were able to withstand severe sulfate attack, but the use of bituminous fly ash led to premature failure.

Understanding the pozzolanic mechanism of CFBC fly ashes in concrete was one of the main components of this research. For this purpose, X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), and thermogravimetric analysis (TGA) was performed on binary paste mixtures containing 20% CFBC fly ash. Hydration of reactive phases (calcined clay, aluminosilica glass, anhydrite, free lime) in CFBC fly ash which made up close to 75% of its mass, resulted in the generation of ettringite, CO₃-AFm (i.e., hemicarboaluminate, monocarboaluminate), and C-A-S-H phases. Bituminous fly ash contributed to greater ettringite and secondary C-A-S-H gel formation, while anthracite fly ash was responsible
for greater AFm phase production. Use of CFBC fly ash led to greater Si/Ca and Al/Ca values for the C-A-S-H phase, compared to the 100% OPC mixture.

Finally, carbon neutralization/reduction techniques were investigated for their efficiency in reducing the interference of CFBC fly ash with air-entraining admixtures (AEA) performance in concrete. Coating of unburned carbon with sacrificial surfactants improved the slump and compressive strength of concrete, but slightly reduced its fresh and hardened air content. Combustion of fly ash at 500°C for 2h was very effective in reducing the AEA uptake by CFBC fly ashes, and increased combustion temperatures did not yield any significant improvements.
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ACKNOWLEDGEMENTS

I would like to express my gratitude to all of those who have helped me during my dissertation. First and foremost, I would like to thank my advisor, Dr. Farshad Rajabipour, for his guidance and patience throughout my graduate career. His immense knowledge and insistence on excellence has had a significant impact on my personal and intellectual growth. I feel very proud to have had him as my mentor and role model. This thesis has also benefited from the valuable feedback and suggestions made by my committee members: Dr. Shelley Stoffels, Dr. Tong Qiu, Dr. Aly Said, and Dr. Barry Scheetz. Thank you for devoting your time and support to this endeavor. I would like to express my special appreciation to Dr. Patrick Fox, without whom I would have not been able to overcome the challenges I faced during this journey. I am thankful to Dr. Steven Feldman (at the National Institute of Standards and Technology), Nichole Wonderling, Julie Anderson, Katya Bazilevskaya (at Penn State’s Materials Characterization Laboratory), and Dan Fura (at Penn State’s Civil Infrastructure Testing and Evaluation Laboratory) for their invaluable insights and technical support. I would also like to acknowledge the American Concrete Institute (ACI) and the Pennsylvania Coal Ash Research Group (PCARG) for their financial support of this research as well as providing valuable technical advice during this project.

I am deeply grateful for my colleagues and friends at Penn State. You have been my support system and family throughout my stay in State College. Maryam and Khashayar, I cannot thank you enough. To my mom and dad, thank you for your unconditional love and support during some of the hardest years of my life. I am incredibly privileged to have been raised in such an intellectual environment, you both inspire me every day. Lastly, to my beloved brother that is unfortunately no longer with us, I love you with all my heart.
Chapter 1

Introduction

1.1 Motivation and Significance

In recent years, reports of fly ash shortages for use in concrete have become more common in the United States [1], [2], [3], [4]. A recent survey by the AASHTO subcommittee on materials [5] of all State Departments of Transportation (DOTs), the Federal Aviation Administration (FAA), and the Army Corps of Engineers showed that the concern with fly ash supply is not a minimal or regional issue, as over 80% of the respondents indicated having issues with fly ash availability over the past 4 years. These supply issues are in part due to a decline in the total quantity of fly ash produced [6] (Figure 1-1) as utilities have shifted fuel sources (e.g., coal to natural gas). They are also due to stricter air pollution and environmental regulations (e.g., [7], [8]), which affect the quality of fly ash by increasing its carbon content (e.g., due to the use of low NOx burners and activated carbon), and calcium and sulfur contents [9][10]. The economic and regulatory incentives have also encouraged the use of low sulfur western coals (yielding Class C fly ash), at the cost of Class F fly ash, with the latter having a superior performance in mitigating alkali-silica reaction (ASR) in concrete [11].

Based on today’s practices and standards, it is estimated that by year 2030, the supply of ASTM C618-compliant fly ash in the United States will be approximately 14 million tons, while the demand will exceed 35 million tons [12]. The shrinking supply of high-quality and economically available fly ash threatens the competitiveness and market share of concrete against other materials such as asphalt (for pavements), steel (for buildings and bridges), and plastics (for pipes). The concrete industry relies on cheap and abundant fly ash for producing economical,
durable, and sustainable (e.g., low CO\textsubscript{2}) concrete [10] [13]. While fluidized bed combustion fly ash is widely available, it is not being used since its performance in concrete is not fully understood, and guidelines (e.g., ACI documents, ASTM specifications) to evaluate and beneficiate this alternative form of fly ash does not currently exist.

Figure 1-1. Statistics on production and utilization of pulverized coal (PC) fly ash and FBC ash (from ACAA [6])

1.2 Research Objectives

This Ph.D. research pursues the following main objectives:

Objective 1: Characterization of as-produced FBC fly ash and its performance in concrete

Literature on the use of FBC fly ash as concrete pozzolan is limited, and lacks a complete evaluation of the physical and chemical properties of FBC fly ash against ASTM C618 [14] – Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. Past
studies have been mainly focused on evaluating the effects of FBC fly ash on the mechanical properties of concrete, and have reported contradictory results. To address these deficiencies, the goal of this study is to present a complete characterization of several CFBC fly ashes produced in Pennsylvania, and to link these properties with important characteristics of concrete. It is worth noting that not all FBC fly ashes are created equal and their composition and properties may vary considerably from one source to another, partly due to differences in their source coal. In this study, two CFBC fly ashes of distinct compositions (originating from anthracite and bituminous coal sources) are evaluated for their physical, chemical, and mineralogical properties and compared against ASTM C618-19 requirements. The fly ashes are then used as partial (20% by mass) replacement of Portland cement in DOT-compliant pavement concrete mixtures, and their impact on the short and long-term performance of concrete is investigated.

**Objective 2: Understanding the hydration mechanism of FBC fly ash in binary cement-based mixtures**

FBC fly ashes possess pozzolanic properties and this research is aimed at understanding the reaction mechanism of FBC fly ash, in the presence of Portland cement and water. Few earlier studies have looked at the hydration of self-cementitious FBC fly ashes in no-cement mortar and paste mixtures. These fly ashes contain high contents of free lime and sulfur, which significantly surpass ASTM C618 limits, and will most likely cause performance complications such as volume instability, undesirable setting, and extreme heat of hydration. As such, use of self-cementitious FBC fly ashes in concrete may not be practical or require extensive beneficiation procedures. In this study, binary mixtures of Portland cement and CFBC fly ash (containing moderate levels of CaO and SO$_3$) are prepared and monitored over a duration of 90 days to evaluate their pozzolanic reactivity and reaction products. The main crystalline phases are identified using XRD testing, while SEM-EDS is used to determine the chemical composition of various crystalline/amorphous
phases (e.g., C-A-S-H, AFt, and AFm phases) within the microstructure. Thermogravimetric analysis is performed on the control and binary mixtures, to quantify the pozzolanic reactivity of CFBC fly ashes, by measuring changes in portlandite content with time.

**Objective 3: Beneficiation of FBC fly ash and its performance in concrete**

The high unburned carbon content, measured as loss-on-ignition (LOI), is a major limiting factor for the use of FBC fly ash in concrete due to its negative effects on concrete air entrainment and workability. Although various beneficiation techniques (e.g., size separation, electrostatic separation, froth flotation, oil agglomeration, chemical passivation and thermal processing [15]) have been successfully used to reduce/neutralize the unburned carbon in conventional PC fly ash, no treatment of this kind has been tested for FBC fly ash. The goal of this study is to evaluate the effectiveness of chemical passivation and Carbon Burn Out (CBO) methods in reducing the interference of FBC fly ash with the performance of air entraining admixture (AEA) in concrete. In the chemical passivation method, the surface of carbon is coated with sacrificial surfactants to prevent it from adsorbing AEA in concrete. As for the CBO approach, fly ash is combusted at temperatures above carbon ignition (460°C) and below glass devitrification (700°C), to reduce the unburned carbon content. The efficiency of the two methods in terms of improving the air-entrainment property of concrete is evaluated using the Foam Index (FI) testing and fresh and hardened air analysis of concrete.

**1.3. Organization of Contents**

This document is organized in 6 chapters, with the above research objectives addressed in chapters 3-5 (Table 1-1). Chapter two provides a background and literature review on coal combustion processes and byproducts with a focus on PC and FBC fly ashes. The current state of understanding and practice with respect to FBC fly ash is summarized, and research needs to facilitate the use of
FBC fly ash as a viable concrete pozzolan is highlighted. In Chapter three, two sources of CFBC fly ash are characterized for their bulk chemistry and mineralogy (using X-ray florescence, batch leaching, and quantitative XRD); unburned carbon (using LOI, and Leco infrared analyzer); physical properties (moisture content, particle size, fineness, particle shape/agglomeration (via SEM), density, soundness, and water requirement); and reactivity (strength activity index, compressive strength of lime-fly ash mortar according to ASTM C593-06, pozzolanic reactivity of lime-fly ash paste according to RILEM TC TRM267). The fresh (slump, fresh air content) and hardened (compressive strength, hardened air content) properties of concrete mixtures incorporating 20% CFBC fly ash are obtained, and mortar samples are tested for their autogenous shrinkage and effectiveness in mitigation of alkali-silica reaction (ASR). Chapter four addresses knowledge gaps regarding the hydration mechanism of FBC fly ash with moderate levels of CaO and SO₃. Binary mixtures incorporating 20% CFBC fly ash as a replacement of cement are prepared and tested for their mineralogy, chemical composition, and pozzolanic reactivity at 1, 7, 28, and 90 days, using XRD, SEM-EDS, and TGA methods. Chapter five investigates the durability of concrete (chloride ion penetration, water sorbtivity) and mortar (sulfate attack, drying shrinkage) mixtures containing 20% CFBC fly ash. Mercury intrusion porosimetry (MIP) and pore fluid extraction tests are used to relate concrete performance to microstructural features such as pore size distribution and pore conductivity. In Chapter six, the effectiveness of chemical passivation and CBO beneficiation techniques on the air entrainment properties of concrete containing CFBC fly ash is evaluated using fresh air and hardened air analysis of concrete and foam index testing. Chapter seven provides a summary of the findings and conclusions of this research study.
Table 1-1. Desired outcomes related to each chapter

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Desired outcomes</th>
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| Chapter 1: Fluidized Bed Combustion (FBC) Fly Ash and its Performance in Concrete | • Characterizing CFBC fly ash for its bulk chemistry, mineralogy, physical properties, unburned carbon content, and reactivity  
• Determining the effect of CFBC fly ash on the fresh and hardened properties of concrete |
| Chapter 2: Understanding the pozzolanic reaction mechanism of FBC fly ash in concrete | • Identifying the main hydration products of mixtures incorporating CFBC fly ash and Portland cement, and monitoring their change over time.  
• Determining the composition of C-A-S-H phase in such mixtures |
| Chapter 3: Performance of FBC fly ash in concrete | • Determining the effects of CFBC fly ash on concrete durability  
• Relating concrete performance to microstructural features |
| Chapter 4: Performance of beneficiated FBC fly ash in concrete | • Evaluating the effectiveness of chemical passivation and CBO beneficiation techniques in reducing the interference of carbon in CFBC fly ash with the performance AEAs in concrete |

1.4. References


Chapter 2

Review on Coal Combustion Processes and the Performance of Raw or Beneficiated Fly Ash in Concrete

2.1. Coal Combustion Technologies

Power generation is the main consumer of energy in the United States, and coal is the second largest fuel source for this sector (i.e., accounting for 27.4% of the electricity generated in the United States in 2018) [1]. According to the U.S. Energy Information Administration’s Annual Energy Outlook 2018 (AEO), coal usage is expected to remain relatively constant through 2050, despite recent wave of coal plant retirements [2] (Figure 2-1). Coal is a combustible sedimentary rock that primarily contains organic carbon, hydrogen, oxygen and lesser amounts of sulfur and nitrogen. Inorganic/non-combustible compounds in coal such as aluminum and silicon oxides (e.g., in the form of clay impurities in coal) constitute the combustion ash, but their concentration is no more than several percentage points of coal. In fact, up to one tenth of the total mass of coal is material with no fuel value. There are two main theories for the formation of coal, based on the origin of vegetation that is later converted to coal. The autochthonous theory [3] is most accepted since it explains the origin of most coals. It states that plant debris accumulate in the bottom of nearby swamps and bogs, where oxygen content is low. The thick layer of partially decayed organic matter, also known as peat, is then covered by sedimentation (e.g., sand or mud) and coal seam is formed. Under gradual heat and pressure, biochemical reactions occur over thousands and millions of years and drive much of the water and other volatiles out of peat, resulting in the formation of various grades of coal (Figure 2-2). This coalification process constitutes three main reactions: microbiological degradation of plant cellulose; conversion of lignin within the plant to humic
substances; and condensation of humic substances to larger coal molecules. Alternatively, the allochthonous theory [3] explains that vegetation is transported by water and then deposited on the bottom of the sea or lake, and later compressed into solid rock. In general, the autochthonous theory refers to sediments that are native to its location, while the allochthonous theory refers to sediments originating from a place other than where it was found.

Figure 2-1. Prediction for U.S. coal consumption according to AEO2018 [4]

Figure 2-2. Coalification process to form coal under high temperature and pressure [5]
Different varieties of coal (i.e., coal types) arise because of differences in the types of plant material, degree of coalification (i.e., coal rank), and range of impurities (i.e., coal grade). The most common classification is that of coal rank, which refers to the degree of coalification (maturity) that has occurred [6]. The different forms of coal in the order of increasing age/maturity are lignite, sub-bituminous, bituminous, and anthracite (Figure 2-3).

A higher coal rank is accompanied by increases in the carbon content and calorific (heat) value, as well as decreases in the amount of moisture and volatile material (carbon oxides, hydrogen, and traces of sulfur and nitrogen compounds). As coal ages, the color changes from brown to jet black, and the coal becomes harder and more brittle, making it more difficult to burn [8]. In the United States lignite and subbituminous coals are considered as low-rank, while bituminous coals and anthracite are classified as high-rank. As for European classifications, lignite is known as brown coal and anthracite and bituminous coals are hard coals. Subbituminous is in some cases considered as hard coal. The distribution of coal ranks within the United States and Pennsylvania, is provided in Figure 2-4 and Figure 2-5, respectively. ASTM D388-17a (Standard Classification of Coals by Rank) defines four major classes of coals, but each are also subdivided into different groups. The higher rank coals are classified based on their fixed carbon and volatile matter content, whereas the low-rank coals are classified in terms of heating value [3]. The different ranks of coal are described in detail below:
Figure 2-4. Distribution of coal ranks within the United States [9]

Figure 2-5. Distribution of coal ranks within Pennsylvania [10]
• Lignite is the lowest rank of coal. It is a peat that has been transformed into a rock, and that rock is a brown-black coal. Lignite has a heating value of less than 8300 Btu/lb (4614 kcal/kg) and is subdivided into Lignite A and Lignite B, on the basis of heating value (Table 2-1). Lignite constituted 9% of the total U.S. coal production in 2017 [11].

• Subbituminous coal is lignite that has been subjected to increased level of organic metamorphism. It has a heating value of 8300-11500 Btu/lb (4614-6393 kcal/kg) and is subdivided into Subbituminous A, Subbituminous B, and Subbituminous C groups on the basis of heating value. Subbituminous coal constituted 45% of the total U.S. coal production in 2017 [11].

• Bituminous coal is the most abundant form of coal in the world that accounted for 46% of the total U.S. coal production in 2017. West Virginia, Illinois, Pennsylvania, Kentucky, and Indiana were the five main bituminous coal-producing states in 2017, contributing to 74% of total bituminous production [11]. There are five main classifications for bituminous coal: low volatile, medium volatile, high volatile A, high volatile B, and high volatile C. The low and medium volatile bituminous coals are classified based on fixed carbon content (69-86 wt%) and volatile matter (14-31 wt%), while high volatile A, high volatile B, and high volatile C bituminous coals are subdivided on the basis of heating value from 10500 to 14000 Btu/lb (5837 to 7783 kcal/kg).

• Anthracite is a hard, black coal that burns with little flame and smoke. It is the highest rank of coal, with fixed carbon content of 86-98 wt% and volatile matter of 2-14 wt%. Anthracite accounted for less than 1% of the coal mined in the United States in 2017 [11]. All of the anthracite mines in the United States are in northeastern Pennsylvania. It is subdivided into semi-anthracite, anthracite, and meta-anthracite on the basis of carbon content. In the U.S., anthracite is mainly used by the metals (e.g., steel) production industry.
Although coal reserves are estimated to last for the next 200 years, many challenges exist regarding efficient and environmentally-friendly use of coal combustion [6]. In conventional pulverized coal (PC) fired boilers, which currently dominate the electric power generation industry, the combustion of fuel takes place at temperatures ranging from 1150°C to 1750°C. This results in high sulfur (SO\(_2\)) and nitrogen oxides (NO\(_x\)) emissions. Removal of such pollutants from the flue gas requires expensive add-on scrubbing and desulfurization units [12], [13]. In an attempt to eliminate the need for external emission control units while fulfilling stricter environmental regulations and enabling the use of coals with high sulfur content, the Fluidized Bed Combustion (FBC) process was developed and became commercially available in the 1970s. This rapidly maturing technology is widely used in Europe, North America, and China among other places [14]. Currently in the United States, there are 18 FBC power plants burning refuse coal (waste coal), 14 located in Pennsylvania,

### Table 2-1. Classification of coal by rank according to ASTM D388-19

<table>
<thead>
<tr>
<th>Class/Group</th>
<th>( \text{FC} \text{vol} \text{MM}, % ) Limits, %</th>
<th>( \text{V}_{\text{m,mag}} \text{MM}, % ) Limits, %</th>
<th>GCV(_{\text{vol}, \text{dry}} \text{ Limits}\text{b}</th>
<th>Btu/lb</th>
<th>MJ/kg\text{c}</th>
<th>Agglomerating Character</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Equal or Greater Than</td>
<td>Less Than</td>
<td>Equal or Greater Than</td>
<td>Less Than</td>
<td>Equal or Greater Than</td>
<td>Less Than</td>
</tr>
<tr>
<td>Anthracite:</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Meta-anthracite</td>
<td>98</td>
<td>98</td>
<td>2</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracite</td>
<td>92</td>
<td>92</td>
<td>2</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Semi-anthracite:</td>
<td>86</td>
<td>92</td>
<td>8</td>
<td>14</td>
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<tr>
<td>Bituminous:</td>
<td></td>
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<tr>
<td>Low volatile bituminous coal</td>
<td>78</td>
<td>96</td>
<td>14</td>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium volatile bituminous coal</td>
<td>69</td>
<td>78</td>
<td>22</td>
<td>31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High volatile A bituminous coal</td>
<td>...</td>
<td>69</td>
<td>31</td>
<td>...</td>
<td></td>
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<tr>
<td>High volatile B bituminous coal</td>
<td>...</td>
<td>...</td>
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<tr>
<td>High volatile C bituminous coal</td>
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<tr>
<td>Subbituminous:</td>
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<tr>
<td>Subbituminous A coal</td>
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<td>Subbituminous B coal</td>
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<td></td>
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<tr>
<td>Subbituminous C coal</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Lignite:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lignite A</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lignite B</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) This classification does not apply to certain coals, as discussed in Section 1.
\(^b\) Refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal.
\(^c\) Megajoules per kilogram. To convert British thermal units per pound to megajoules per kilogram, multiply by 0.0023255.
\(^d\) Agglomerating, classify in low volatile group of the bituminous class.

It is recognized that there may be non-agglomerating varieties in these groups of the bituminous class, and that there are notable exceptions in the high volatile C bituminous group.
Refuse coal refers to any by-product of coal mining or coal cleaning operations with an ash content greater than 50% (by weight) and a heating value less than 6000 Btu/lb (13900 kJ/kg) [16]. In addition to waste coal, the FBC technology is well suited to the utilization of coke, petroleum coke, oil shale, biomass, some types of municipal solid waste, sludge, etc. [17]. The PC and FBC combustion technologies, and their products are explained in detail in the following sections.

2.2 Suspension Firing of Pulverized Coal (PC) and Its Products

Suspension firing is the most commonly used method for burning coal to generate electricity. In PC boilers, coal is grinded in mills to a fine powder (e.g., 65% to 85% of the particles passing No. 200 sieve) and then pneumatically transported, with approximately 10% of the combustion air, through the burners into the furnace. There, the pulverized coal is combusted in suspension, with continuous mixing of fuel and air (Figure 2-6).

In PC boilers, pulverized coal is combusted at temperatures ranging from 1150°C to 1750°C, depending largely on the coal rank [12]. At such high temperatures, coal undergoes two main combustion mechanisms of devolatilization (i.e., release of volatile organic constituents in a matter of milliseconds), and char oxidation (i.e., a series of carbon-oxygen reactions). The latter reaction is relatively slower and in the order of several seconds. This results in melting of the majority of mineral impurities (e.g., clays) that are present in the coal. These molten droplets will subsequently solidify in the flue gas, primarily in the form of alumino-silica glass spheres, which make up the resulting fly ash. Other main combustion products in a PC boiler include bottom ash, boiler slag, and flue gas desulfurization (FGD) products. These are introduced in the following sections.
2.2.1. Pulverized Coal (PC) Fly Ash

The majority (i.e., up to 70%) of fly ash is separated from the flue gas using filters or other particulate removal units located at the boiler outlet [3]. The main types of particulate removal filters used in PC furnaces are electrostatic precipitators, bag houses, and cyclones. Electrostatic precipitators (ESP) are particle removal devices that use high voltage electrodes to create an electrical field and force charged particles out of the stream of flue gas and onto collector plates (Figure 2-7). Although the collection efficiency of ESP may be 99% or higher, its performance is affected by the flue gas properties, especially the electrical resistivity of particles [19]. A more effective method of separating particles from flue gas, with guaranteed collection efficiency greater than 99%, is using baghouse filters. Most baghouses use an array of long and narrow cylindrical shaped fabric bags as a filter medium. As the flue gas is blown through the bags using fans, the solid particles get trapped inside, and clean air passes through. Once there is sufficient drop in pressure, the bag cleaning process begins and the resulting fly ash is collected in hoppers (Figure 2-8). Cyclones are the third and a less efficient method of particulate removal compared to the
previous techniques. They are typically used as pre-cleaners, and are followed by electrostatic precipitators and/or baghouses. Cyclones create a vortex which causes larger particles within the flue gas to move outwards and hit the chamber wall, where they slide down into hopper at the bottom of the cyclone. The clean air continues to move upwards in a narrow spiral, and finally exits the outlet at the top (Figure 2-9).

Figure 2-7. Electrostatic precipitators (ESP) used for separating fly ash from the flue gas [20]

Figure 2-8. Baghouse filters used for separating fly ash from the flue gas [20]
Rapid cooling of fly ash within the flue gas results in the formation of solid spherical particles (0.5 to 300 µm in diameter) as well as hollow cenospheres (empty shells) and pleurospheres (shells containing smaller fly ash particles) as shown in Figure 2-10. The bulk chemistry of the fly ash is a function of feed coal (Table 2-2), the pulverizing process and combustion conditions. Its principal constituents include SiO₂ (35 to 60 percent), Al₂O₃ (10 to 30 percent), Fe₂O₃ (4 to 20 percent), and CaO (1 to 35 percent) (Figure 2-11) [21]. Coals that contain relatively small amounts of calcium, for example anthracite, bituminous, or some lignite coals, results in ASTM C618 Class F fly ash. This class of fly ash primarily contains amorphous aluminosilicate particles as well as spherical iron oxide particles (Figure 2-12). Subbituminous and some lignite coals contain larger amounts of calcium and produce calcium aluminosilicate glass phases in the fly ash [21].
Figure 2-10. Left: hollow cenosphere fly ash, right: pleurosphere fly ash containing smaller spheres [22]

Table 2-2. Normal range of chemical composition for fly ash produced from different coal types (expressed as percent by weight) [23]

<table>
<thead>
<tr>
<th>Component</th>
<th>Bituminous</th>
<th>Subbituminous</th>
<th>Lignite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>20-60</td>
<td>40-60</td>
<td>15-45</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>5-35</td>
<td>20-30</td>
<td>10-25</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>10-40</td>
<td>4-10</td>
<td>4-15</td>
</tr>
<tr>
<td>CaO</td>
<td>1-12</td>
<td>5-30</td>
<td>15-40</td>
</tr>
<tr>
<td>MgO</td>
<td>0-5</td>
<td>1-6</td>
<td>3-10</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0-4</td>
<td>0-2</td>
<td>0-10</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0-4</td>
<td>0-2</td>
<td>0-6</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0-3</td>
<td>0-4</td>
<td>0-4</td>
</tr>
<tr>
<td>LOI</td>
<td>0-15</td>
<td>0-3</td>
<td>0-5</td>
</tr>
</tbody>
</table>

Figure 2-11. CaO–Al$_2$O$_3$–SiO$_2$ ternary diagram of cementitious materials, including Class F and Class C fly ash [24]
For use in concrete, PC fly ash must comply with the requirements of ASTM C618. The chemical requirements stated by this standard are a maximum SO$_3$ content of 5%, maximum moisture content of 3%, maximum LOI value of 6%, as well as a minimum SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$ content of 70% and 50% for Class F and C fly ash, respectively. The use of Class F fly ash containing up to 12.0% LOI may be approved by the user if either acceptable performance records or laboratory test results are made available. With regards to physical requirements, maximum fineness of 34%, minimum strength activity index (at either 7 or 28 days) of 75%, maximum water requirement of 105%, and maximum autoclave expansion of 0.8% are required. Some optional requirements such as the magnitude of drying shrinkage, uniformity requirements regarding the use of air-entraining admixtures, and sulfate resistance, may also be applied when specifically requested.

According to ASTM C618-19, PC fly ash is classified based on its bulk chemistry as Class F (when mass fractions of SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$>70%) or Class C (when mass fractions of SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$>50%). Class C fly ash has greater calcium oxide content than Class F fly ash (approximately CaO>20). Generally, the higher the content of CaO, the lower SiO$_2$+Al$_2$O$_3$+ Fe$_2$O$_3$, and the greater the amount of SO$_3$ and alkalis (Na$_2$O and K$_2$O) within the fly ash. Furthermore, LOI is higher for Class F fly ashes than Class C because of the presence of more unburnt carbon.
Low calcium fly ash (Class F) primarily contains alumino-silicate glass, and lesser quantities of mineral phases, including quartz (SiO$_2$), mullite (3Al$_2$O$_3$·2SiO$_2$) and iron oxides (Fe$_2$O$_3$, Fe$_3$O$_4$) [27]. Mullite is found in substantial quantities only in low calcium fly ashes and accounts for the majority of alumina in fly ash but is not normally chemically reactive in concrete [21]. High calcium fly ash (Class C) contains the previously mentioned phases, and may also contain additional crystalline phases such as anhydrite, alkali sulfate, dicalcium silicate, tricalcium aluminate, free calcium oxide, and melilitite [28]. When used in concrete, Class F fly ash primarily acts as a pozzolan (i.e., “siliceous or silico-aluminous material that in itself possesses little or no cementitious value, but that will, in finely divided form and in the presence of moisture, chemically reacts with calcium hydroxide at ordinary temperatures to form compounds having cementitious properties” [29]). Meanwhile, Class C fly ash has both hydraulic (i.e., the ability to set, harden, and gain strength as a result of chemical reactions with water, in the absence of Portland cement) and pozzolanic properties [30] [31] [32]. This is because the content of silica and alumina, which are the primary contributors to the pozzolanic reaction in concrete, are greater in Class F fly ash while CaO, having hydraulic properties, are more abundant in Class C fly ash. Silica and alumina combine with lime and water to form calcium silicate hydrate (C-S-H) and calcium aluminate hydrates (e.g., AFm phases) [21].

Partial replacement of cement with fly ash has been proven to increase the workability, water and chloride ion penetration resistance, and later-age strength of concrete, as well as, to reduce the heat of hydration, shrinkage and alkali silica reactivity. Other than its use in concrete, PC fly ash can be used in a range of other applications, including structural fill materials (e.g., embankments), soil and road base stabilization, and mine reclamation [31].
2.2.2. Other PC Combustion Products

The bottom ash and boiler slag are the un-combusted material that accumulate at the bottom of the boiler and are fairly similar in composition to fly ash (Figure 2-13). PC boiler units are classified as either dry bottom or wet bottom, depending on whether the bottom ash is removed in a solid or molten state. The majority of PC boilers operate with dry bottom units; i.e., they produce bottom ash. In the wet bottom units, the combustion temperature exceeds that of ash melting point; as such, they produce boiler slag [32]. Because of the higher content of fly ash in dry bottom furnaces, these boilers are larger and more expensive than wet bottom furnaces. However, they are simpler to operate and more flexible with regards to the fuel source [3].

The bottom ash is quite angular, with a large particle size (usually with 50 to 90 percent passing a 4.75 mm sieve and 0 to 10 percent passing a 0.075 mm sieve) and porous structure. Bottom ash can be used as fine aggregates in concrete, fill, anti-skid, and sand blasting applications. The porous structure of bottom ash makes it lighter and less durable than conventional aggregates [34]. If grinded, bottom ash can also be used as a filler material to partially replace Portland cement in concrete [31]. As for boiler slag, once the molten slag is quenched with water, it fractures, crystallizes, and forms pellets. These hard, angular particles have a smooth glassy appearance and
can be used as blasting grit and roofing granules, mineral filler in asphalt, fill material for structural applications, mineral additive in concrete, and snow and ice traction control material. Recently, the supply of boiler slag has declined due to the shutdown of wet bottom boiler power plants [34].

In addition to particulate matter (i.e., fly ash), other harmful emissions must be prevented or separated from the flue gas before it is released to the atmosphere. Most importantly, SOx and Hg must be removed while the formation and emission of NOx, ozone, and lead (Pb) must be mitigated.

To control SOx emission, lower sulfur coals can be used, the fuel can be cleaned from sulfur-bearing compounds (e.g., pyrite) prior to combustion, or flue gas desulfurization (FGD) units can be used after particulate removal units to separate sulfur oxides from flue gas (Figure 2-6). During combustion, most of the sulfur content in coal is converted to SO2 and a small percentage is oxidized to SO3 [32]. The Clean Air Act and Amendments of 1990 (1990 CAAA) requires major reductions in sulfur oxide (SO2) and nitrogen oxides (NOx) emissions, the pollutants that cause acid rain [3]. That is why most coal combustion facilities which use high-sulfur coals, decided to add flue-gas scrubbing systems [32]. The most widely used FGD units are the wet scrubbing systems. In these units, a limestone (CaCO3) or lime (Ca(OH)2) slurry is sprayed onto flue gas to transform SO2 to sulfite hemi-hydrate (CaSO3·½H2O), which is further oxidized to synthetic gypsum (CaSO4·2H2O) [32]. This process removes more than 90% of the SO2, however it does not prevent the majority of SO3 from being released into the atmosphere [32]. Also, CO2 is produced as a by-product of the limestone calcination. The resulting scrubber sludge can be disposed in slurry ponds, or is dewatered and landfilled. Where a higher quality synthetic gypsum is produced, it can be used for Portland cement or wallboard manufacturing [3]. For dewatering, hydrocyclones and vacuum filters are employed to reduce the moisture content of the slurry to less than 10% [3].

A less common type of FGD units is the dry scrubbing systems, including spray dry scrubbers and sorbent injection processes [3]. These FGD units are placed before particulate
removal units and produce dry FGD products that are collected together, and are as such comingled with, fly ash. As a consequence, the resulting fly ash has a high sulfur content and is usually unusable for concrete applications. A particular type of dry scrubber that has recently gained popularity is the dry sorbent injection (DSI) process. Here, dry hydrated lime or sodium-based sorbents (e.g., trona) are injected into humidified (~100% RH) flue gas to form sulfites and sulfates of calcium or sodium. The unused sorbent, FGD products, and fly ash are subsequently collected in the particulate control units. In this case, the resulting fly ash has high contents of sulfur, calcium, and/or sodium.

To reduce the amount of NOx in the flue gas, two main approaches can be taken: furnace combustion modification, which includes the use of low-NOx burners; and ammonia (or urea) injection with or without catalysts. In the first method, combustion is performed at different stages, meaning that at certain areas of the furnace, the oxygen level is kept low, and at later stages, air is added to complete combustion. One of the main challenges of this technique is ensuring complete fuel combustion whilst limiting the amount of NOx formation [35]. Also, such low oxygen conditions may increase unburned carbon content and its reactivity in the resulting fly ash. The carbon (measured as LOI) associated with a low-NOx fly ash has a greater propensity to adsorb liquid chemical admixtures used in concrete, especially the AEA. This can lead to relatively large increases in the AEA dosage requirement in concrete [21].

The most common ammonia (or urea) injection technology is the selective catalytic reduction (SCR) method which reduces the amount of NOx by oxidation/reduction reactions between ammonia and NOx, in the presence of a catalyst. The main concern with this technique is the amount of unreacted ammonia (also known as ammonia slip) in fly ash, which may be released in the form of vapor when in contact with water, causing odor issues. Furthermore, ammonia can affect the leaching of trace elements in fly ash. However, since most modern SCR systems limit
the ammonia slip content to less than 2 ppm, the effect of unreacted ammonia on fly ash performance in concrete is negligible [35].

The most common technologies for mercury capture, with the least negative impacts on coal combustion products are: sorbent injection and co-removal with fly ash; and mercury oxidation and co-removal with FGD solids. Powder activated carbon, referring to the product of heat- and steam treatment on carbon-based materials, is the most common sorbent for mercury removal. This highly porous powder can effectively absorb mercury and is later removed from the flue gas along with fly ash. The captured carbon may adversely affect the properties of fly ash in concrete, especially with regards to the increased AEA demand. Other sorbents such as specialty activated carbon and non-carbon are advantageous, since they preserve the quality of fly ash. As for the mercury oxidization technique, chemical addition (typically using halogen) or the catalysts from the SCR method are used to oxidize mercury so it can be removed with the FGD solids. Oxidized mercury is desired since it is soluble and can be removed from the downstream scrubber systems. This is not the case for elemental mercury, which is in fact the predominant form. Although some drawbacks of this method are increased mercury and halogen concentrations in the resulting fly ash, these effects are insignificant compared to that of activated carbon injection [35].

2.3. Fluidized Bed Combustion (FBC) and Its Products

In an attempt to eliminate the need for external emission control units while fulfilling stricter environmental regulations and enabling the use of coals with high sulfur contents, the fluidized bed combustion process was developed and commercialized in the 1970s. FBC is a combustion technology suitable for burning extremely low-grade coal (refuse coal) for power generation, with the environmental benefit of cleaning up acid mine drainage (AMD)-producing gob piles (piles built of accumulated waste rock, removed during coal mining, that can leach acid mine water and
hazardous substances into water sources). In this method, sulfur-absorbing materials (e.g., limestone or dolomite) are added in a powder form to the fuel along with an inert material (e.g., sand or ash) inside the boiler. The mixture is fluidized using air jets and combusted at temperatures ranging from 750°C to 900°C. Fluidization refers to the dynamic fluid-like state of the solid-air mixture within the furnace, which is caused by the passage of upwards jets of air through the granular material. The main purpose of the inert material is to improve mixing and heat transfer among different components, while the sulfur-sorbent is used to minimize SO\(_x\) emissions in the flue gas. Depending on the sulfur content of the fuel, the sorbent may comprise up to 50% of the bed inventory [3]. The temperature of the furnace is high enough to allow calcination of limestone and combustion of coal [3], but does not result in melting of clays and other mineral matter. Temperatures are well below the threshold of nitrogen oxidization (i.e., 850 °C), and creation of thermal NO\(_x\) [12],[13],[36]. The temperature range is chosen to ensure that the reactions between SO\(_2\) and sorbent are thermodynamically and kinetically balanced [3]. It is worth noting that the low combustion temperatures of FBC boilers affects their electricity generation capacity. While FBC powerplants are typically up to 300 MW in size, and can be as high as 400-600 MW, PC power plants can exceed size of 2000 MW [37].

During the FBC process, initially, limestone is thermally decomposed (calcined per Eq. 2-1), and porous CaO particles are formed. A significant fraction (approximately 70%-80%) of this CaO combines with SO\(_2\) emissions and CaSO\(_3\) (calcium sulfite) is formed (Eq. 2-2) [38]. In the presence of abundant oxygen, anhydrite (CaSO\(_4\)) is produced from the oxidization of CaSO\(_3\) (Eq. 2-3) [13]. As high as 95% of the sulfur in coal is captured during these reactions.

\[
\text{CaCO}_3 + \text{heat} \rightarrow \text{CaO} + \text{CO}_2 \quad \text{(Eq. 2-1)}
\]

\[
\text{CaO} + \text{SO}_2 \rightarrow \text{CaSO}_3(s) \quad \text{(Eq. 2-2)}
\]

\[
\text{CaSO}_3(s) + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4(s) \quad \text{(Eq. 2-3)}
\]
In addition to lower overall SO$_x$ and NO$_x$ emissions, FBC enables energy efficient combustion and the use of both high and low-grade coals, as well as partial replacement of coal with biomass. During the combustion, upwards jets of air cause the solids (pulverized fuel, limestone, and sand) to be suspended, ensuring the gas and solids mix together turbulently for better heat transfer and chemical reactivity. In fluidized bed combustion, the solid concentration is significantly greater than that of PC boilers, and therefore convective heat transfer dominates over radiation [3]. This significantly reduces the size of FBC furnaces. Furthermore, the elutriation of particles (i.e., separation of particles based on their size using a stream of gas or fluid flowing in a direction usually opposite to the direction of sedimentation) at high velocities yields high amounts of fly ash (60-80 wt% of the total ash produced) versus bottom ash [39][40]. Similar to PC combustion, fly ash is collected using de-dusting systems such as electrostatic precipitators, cyclones, and bag filters.

To further increase the gas-solid contact time, the CFBC technology was developed in the late 1970s as a subcategory of FBC boilers. Its basic concept is using high gas velocities to entrain a considerable portion of the heavier particles and carry them out of the boiler. The solids are then separated from the flue gas in one or more recycling cyclones and returned to the combustion bed, thus preventing unburnt fuel from leaving the furnace (Figure 2-14). This creates a recycling loop through which fuel particles can pass 10 to 50 times until near-complete combustion is achieved [41]. The prolonged combustion time also ensures that lower combustion temperatures compared to conventional FBC and PC boilers can be used. In comparison with conventional FBC, the CFBC technology allows a better combustion efficiency, smaller combustor size, simpler fuel feed system, lower SO$_x$ and NO$_x$ emissions, lower limestone consumption and in turn, lower CaO content in the ash, and lower unburned carbon and loss-on-ignition (LOI) in the ash [12].

The Pressurized Fluidized Bed Combustion (PFBC) technology, which operates at elevated pressures (4 to 30 atmospheres) rather than atmospheric conditions, also provides similar benefits
as CFBC. In the PFBC process, the CaO in the combustion residue tends to stay in the form of calcite, rather than in the form of free lime, due to the higher CO$_2$ partial pressure in the combustor [13]. Therefore, the content of free lime in PFBC ash is significantly lower than that of FBC ash, and this results in low ettringite formation when the ash is used in concrete [40]. Finally, the pressurized circulating FBC (PCFBC) is the combination of CFBC and PFBC [3].

![Figure 2-14. Schematic of circulating fluidized bed combustion (CFBC) unit [42]](image)

FBC fly ash and bottom ash constitute approximately 13wt.% of the annual 111 million tons of coal combustion products (CCPs) produced in the United States [43]. Other main CCPs include PC fly ash (~34wt.%), FGD materials (~47wt.%), bottom ash (~9wt.%), and boiler slag (~2wt.%) [44]. Roughly 60 – 80 % of the total FBC ash is fly ash, the rest being bottom ash. FBC fly ash has a similar bulk chemistry (with respect to major elements) to conventional PC fly ash, except for the absence of mullite which is a product of coal combustion at 1500°C [45]. FBC fly ash primarily contains crystalline and amorphous alumina-silica phases (e.g., calcined clays), quartz, anhydrite, iron oxide, calcite, and free lime [45]. However, due to the lower combustion temperature of FBC
boilers, the ash-forming minerals in coal are not melted but de-hydroxylated (e.g., calcined clays), resulting in a fly ash with sub-angular particles [46] (Figure 2-15). These particles also have internal porosity, resulting in up to 5× the surface area of PC fly ash, and this contributes to their reactivity and also increased water demand [27].

![Figure 2-15. SEM/EDS images of (left) PC fly ash (right) FBC fly ash [47]](image)

FBC bottom ash is coarser, with lower fixed carbon (i.e. solid combustible residue that remains after a coal particle is heated and the volatile matter is expelled), and hematite (Fe₂O₃) content [48] [49]. Anhydrite is the most abundant crystalline component in FBC ash and its amount in bottom ash is expected to be higher than that of FBC fly ash [49]. In most cases, the content of SO₃ and free lime is also greater in bottom FBC ash [50]. Some of the applications of FBC ash include surface and subsurface mine reclamation, soil stabilization, road base, structural fill, and synthetic aggregate [31] [30]. However, the majority of FBC ash is disposed in dedicated landfills [31].

2.3.1. Hydration Mechanism of FBC Fly Ash in Concrete

FBC fly ash is reported to have self-cementitious properties due to its high contents of f-CaO (free lime) and SO₃ [51], [52], [53], [54], [55], [56], [57], [58], [46], [59], [60], [61]. To increase the SO₂-removal efficiency, the ratio of Ca/S is often increased in the boiler to 2.0–2.5, resulting in high amounts of unreacted lime and anhydrite remaining in the fly ash [62]. The higher content of
\( f \)-CaO and SO\(_3\) is beneficial to the generation of C–S–H and AFt phases \([58]\), enabling non-Portland cement concretes with compressive strengths similar to that of Portland cement concrete \([57]\).

Earlier studies have looked at the hydration of FBC fly ash in non-Portland cement mortar \([57]\) and paste \([58], [46], [59], [60], [61]\) mixtures. They observed X-ray diffraction peaks of AFt, portlandite, gypsum, calcium silicate hydrate \([59], [46], [58], [57]\), quartz, calcite \([57] [61]\), and calcium alumino-silicate hydrate \([57]\). The self-cementitious properties of FBC fly ashes used in these studies was made possible due to their high CaO (15-45%) and SO\(_3\) (5-25%) contents.

FBC fly ash has been shown to contain great amounts of dehydroxylated clays, an abundant source of both silica (SiO\(_2\)) and alumina (Al\(_2\)O\(_3\)). When calcined clays are used separately as a partial replacement for Portland cement, the reaction products consist mainly of amorphous calcium aluminosilicate hydrates (C-A-S-H), and crystalline products such as calcium aluminate hydrates (C-A-H), C\(_2\)ASH\(_8\), C\(_4\)AH\(_13\) and C\(_3\)AH\(_6\) \([63][64]\). If carbonation is not restricted, carbo-aluminates may also be produced \([65]\). However, reports of C-A-S-H phases among the hydration products of FBC fly ash has been scares \([57]\). In the study by Iribarne et al. \([57]\), fragments of mortar beams (cured for 896 to 1114 days) with 75 wt.% of sand as inert material and 25 wt.% of CFBC fly ash as binder, were ground and the light fractions (separated by density) were analyzed using XRD. Minor peaks of various crystalline hydrated Ca-Al silicates (CaAl\(_2\)(SiO\(_3\))_4.6H\(_2\)O and CaAl\(_2\)Si\(_{10}\)O\(_{24}\).7H\(_2\)O) were detected. Due to ineffective separation of sand particles, significant amounts of non-reactive quartz were also observed. Despite the presence of ettringite and portlandite in previous studies, these hydration products were missing in numerous samples. Moreover, no AFm species were detected, possibly as a result of the absence of cement in the mix.

Considering that most state DOTs in the U.S. strongly encourage partial replacement of Portland cement with fly ash or slag, and that the future supply of these pozzolans is not keeping up with demand, the use of FBC fly ash as a concrete pozzolan merits attention. To safely and properly use FBC fly ash in concrete, its pozzolanic reaction and other interactions with Portland
cement shall be investigated. Identifying and monitoring the reaction products in cement-FBC fly ash mixtures will be beneficial in understanding the effect of FBC fly ash on the short- and long-term performance of concrete.

2.3.2. Performance of FBC Fly Ash in Concrete

The use of FBC fly ash in concrete is not without potential challenges, as ASTM C618 [66] currently excludes FBC fly ash from its scope. Based on the available literature, FBC fly ash may have high sulfur (SO$_3$), free CaO, and unburned carbon (LOI) contents [67],[68]. SO$_3$>5 wt% may cause flash setting and abnormal expansion at early ages, due to ettringite formation. Similarly, hydration of free CaO can cause excessive heat and volume instability [31]. The LOI may vary from a few tenths of percent to more than 10%, and this impacts the workability and air entrainment performance of concrete mixtures [40],[69],[70],[71].

Studies on the use of FBC fly ash in concrete have been limited, and reported contradictory results. Havlica et al. [13] showed that mortars containing pressurized FBC ash or conventional FBC ash can produce similar or better strength in comparison with ordinary Portland cement (OPC) mortars after only 3 days of hydration. Nguyen et al. [72] studied a high volume fly ash (HVFA) cement paste and reported improved mechanical properties (compressive strength, dynamic Young’s modulus, shear modulus, and ultrasonic wave velocity) when up to 5% of Class F fly ash was replaced with CFBC fly ash. Glinicki et al. [73] showed that CFBC fly ash reacts pozzolannically with portlandite and also produces a slightly higher quantity of ettringite as a result of its SO$_3$ content. On the other hand, Gazdić et al. [45] compared the performance of FBC fly ash to PC fly ash at 15% and 30% cement replacement levels and reported a reduced strength in mixtures containing FBC fly ash compared to those with PC fly ash or straight OPC. Wu et al. [74] studied mortars containing Class F and/or CFBC fly ash and reported a reduced 28-day strength, delayed setting, and length expansion in mortars with CFBC fly ash. The latter was attributed to
the higher SO$_3$ content of the CFBC fly ash. Robl et al. [75] reported both an increase and a decrease in mortar strength with the partial replacement of cement with CFBC fly ash, depending on the source of cement.

In addition to the contrary results for compressive strength, very little literature is available on the effect of FBC fly ash on concrete durability. Chi and Huang (2014) [76] evaluated the performance of concrete mixtures containing Class F fly ash and CFBC fly ash (30% PC + 20% CFBC, 50% PC + 20% CFBC) against water permeability (CNS 3763), chloride ion penetration (ASTM C1202), sulfate attack (ASTM C88), and carbonation. The results were compared with mixtures containing Class F fly ash (50%) and that of the control (100% OPC). Although tertiary mixtures (containing PC and CFBC fly ash) had the best performance in terms of resistance to sulfate attack, and water and chloride ion penetration, replacement of cement or Class F fly ash with CFBC fly ash increased both water and chloride ion permeability. An increase in carbonation depth was reported with the use of both fly ashes. In another study by Chi and Huang (2014) [77], the effect of CFBC fly ash (5%, 10% and 15%) on the water absorption (ASTM C642), initial surface absorption (BS 1881-208), sulfate attack resistance (ASTM C88), compressive strength (ASTM C39), and splitting tensile strength (ASTM C496) of roller compacted concrete was investigated. Results showed an adverse effect on water absorption with an increase in CFBC fly ash content. Low dosages (5%) of CFBC fly ash reduced initial surface absorption and increased the strength (compressive and tensile), while higher replacement levels (10 and 15%) improved sulfate resistance. It must be noted that the CFBC fly ash used in both studies contained very high contents of sulfur and lime (SO$_3$>29, CaO>55), and low amounts of SiO$_2$ and Al$_2$O$_3$, which is not representative of a typical CFBC fly ash composition. Jóźwiak-Niedźwiedzka [78] reported lower chloride diffusion coefficient (NordTest Build 492) and higher resistivity for concretes containing 15% and 30% CFBC fly ash. However, 30% replacement of cement with CFBC fly ash increased the surface scaling of concretes exposed to cycles of freezing and thawing. Similarly, Glinicki and
Zielinski [79] showed that the use of 20%, 30%, and 40% CFBC fly ash resulted in a scaling degradation of concrete. The effect was pronounced with increasing dosages of CFBC fly ash and its unburned carbon content.

2.3.3. Beneficiation of FBC Fly Ash

Currently, no techniques have been specifically aimed at reducing or modifying the unburned carbon content in FBC fly ash in order to prevent its interference with the air-entraining admixtures in concrete. Earlier studies have investigated the use of screening (dry sieving), hydraulic classification (wet sieving), mechanical activation (grinding), chemical activation, and prehydration of CFBC fly ash to improve the compressive strength and/or volumetric expansion of concrete mixtures. Rolb et al. [27] showed that hydraulic classification and screening (75 μm) of CFBC fly ash can help remove coarser size fractions and improve its performance in mortar in terms of compressive strength. The French patented CERCHAR technology [31] was used to pre-hydrate lime in FBC fly ash, whilst preventing the conversion of anhydrite to gypsum and ettringite. This method was able to significantly reduce the CaO content from 13% to 0.5%, but had slight negative effects on LOI, compressive strength, and permeability. The Polish company named Energomar-Nord, Ltd. [80] used mechanical activation (grinding) of fly ash to improve the compressive strength of concrete. Li et al. [46] showed that the combination of grinding and chemical activation (1% alkali-activated activators, and/or 0.8% mixture of naphthalene-based water reducer with adjustable solidification agent) of fly ash had the best effect in improving the pozzolanic reactivity index of CFBC fly ash, while reducing its water requirement. Zhai et al. [67] also reported a reduction in particle angularity and water requirement (over 10%) of CFBC fly ash, with increased grinding time. However, this process increased the amount of f-CaO content by up to 25%. The CaO present in CFBC fly ash is in the form packed with CaSO$_4$ and grinding can help crush the CaSO$_4$ layer, releasing CaO.
Some of the popular techniques for the removal or modification of unburned carbon from PC fly ash include size separation, electrostatic separation, froth flotation, oil agglomeration, chemical passivation and thermal processing [81]. Considering that most of these methods have been commercialized for PC fly ash, it is beneficial to investigate their effectiveness for high LOI FBC fly ash.

2.4. References


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Chapter 3

Characterization of Circulating Fluidized Bed Combustion (CFBC) Fly Ash and Its Performance in Concrete

3.1. Abstract

Concerns over the availability and quality of conventional fly ash for use in concrete has become widespread in recent years. Fluidized bed combustion ash, with its annual U.S. production exceeding 14 million tons, could serve as a reasonable alternative. In this study, two compositionally-different fly ashes from CFBC power plants were evaluated for their compliance with ASTM C618 standard and their impact on the fresh and hardened properties of concrete. The pozzolanic reactivity of the fly ashes was also quantified based on the emerging RILEM test method. These fly ashes met the chemical and physical requirements of ASTM, except for elevated LOI (in both fly ashes) and elevated SO₃ (in one fly ash). Despite this, concrete with proper slump, air content, and strength development could be produced by proper dosing of chemical admixtures. The elevated SO₃ was found not to produce deleterious expansions.
3.2 Introduction

FBC fly ash is a potentially valuable pozzolan that is available at little cost and in large volumes. It is currently a landfilled material. Given the recent shortage in the availability of conventional PC fly ash [1],[2],[3], it is logical to methodically research the composition, structure, and properties of FBC fly ash to determine which fly ash compositions may be usable as concrete pozzolan. Proper characterization of FBC fly ash and its performance in concrete can facilitate development of specifications and guidelines for evaluation, beneficiation, and use of this potentially valuable pozzolanic material.

To address objective 1 of this research (as elaborated on in Chapter 1), two different CFBC coal fly ashes were evaluated for their compliance against ASTM C618 (equivalent to AASHTO M295) standard and their impact on the fresh and hardened properties of concrete. This is the first study in its kind to present a complete evaluation of the physical, chemical, and mineralogical properties of CFBC fly ashes produced in the United States and to link these properties with important characteristics of concrete beyond strength development. The fly ashes were sourced from two CFBC power plants in Pennsylvania that use anthracite or bituminous refuse coal as a fuel source. These power plants generate over 2.0 million tons of CFBC fly ash per year.

3.3 Experimental Procedures

Two sources of CFBC fly ash, byproducts of anthracite and bituminous refuse coal combustion, were acquired, homogenized, and characterized for their physical properties, bulk chemistry, mineralogy, and pozzolanic reactivity. Areas of noncompliance with ASTM C618-19 were identified. Further, the performance of these fly ashes in mortar and concrete mixtures was evaluated by measuring the fresh properties (slump and fresh air content), and hardened properties
(strength development, hardened air structure, autogenous expansion, and ASR mitigation efficiency) of these mixtures.

3.3.1 Physical Properties and Unburned Carbon

Both CFBC fly ashes were characterized for their as-received moisture content (ASTM C311-17), particle size distribution (PSD using laser diffraction), fineness (ASTM C430-17), density (using helium pycnometer), particle shape/agglomeration (via SEM), water requirement (ASTM C311-17), soundness (ASTM C151-18), loss on ignition (ASTM C311-17), and carbon and sulfur contents (using infrared LECO analyzer). Two samples were tested per fly ash for each of the above tests (excluding the water requirement which was based on one sample). The results are reported as the average of the two samples. To achieve proper fineness, the anthracite CFBC fly ash passing #140 sieve was used in all tests. The bituminous CFBC fly ash was tested as received.

The SEM samples were prepared using a mixture of low-viscosity epoxy and fly ash (1:1 mass ratio) embedded in a molded epoxy disk, 25 mm diameter and 12.5 mm height, using a protocol similar to [4]. The samples were polished down to 0.25 μm, and carbon coated before imaging. Thermo Scientific™ Q250 Analytical SEM was used and operated at 10.4 mmHg, 15kV accelerating voltage, and ~10 mm working distance. Backscattered electron (BSE) images were obtained at 1000x magnification. Laser diffraction 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 of fly ash in water. A small amount (~0.03 g) of fly ash 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, as reported by [5]. 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 fly ash. In this technique, the sample
was combusted in air up to 1450°C inside the furnace, and the emitted CO\textsubscript{2} and SO\textsubscript{2} gases were measured separately using infrared detectors.

**3.3.2 Bulk Chemistry and Mineralogy**

X-ray fluorescence (XRF) analysis was conducted on fly ash samples to determine their bulk chemistry. Homogenous fused glass beads were prepared by heating a mixture of fly ash and lithium borate (flux) to 1000°C. XRD with Rietveld refinement was performed to identify and quantify the mineral and amorphous phases present in each fly ash. Fly ash samples were ground to less than #400 sieve, mixed with 15% internal standard (highly crystalline ZnO), and placed on spinner stage rotating at 4 rev/s. The incident X-ray beam was Cu K\alpha radiation (\(\lambda=1.5419\ \text{Å}\)) produced using 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° 2\theta with step size of 0.02°, for a total scan time of ~30 min. A PIXcel detector in scanning line mode was used.

To monitor the dissolution rate of soluble species from CFBC fly ash into concrete pore solution, batch leaching tests were carried out. Of special interest was the solubility of sulfur compounds (e.g., anhydrite), which can lead to formation of ettringite and potential undesirable setting or expansion. In the leaching test, CFBC fly ash was exposed to synthetic concrete pore solution. The concentrations of S, Si, Al, Ca, Na, and K in the solution were measured at 1, 3, and 7 days of exposure. The results were compared with the concentrations obtained from the leaching test of type I/II Portland cement (with composition reported in Table 3-5). The synthetic pore solution was prepared by mixing 0.2 mol/L NaOH and 0.5 mol/L KOH with saturated lime water to reach a pH of 13.85. Next, fly ash or Portland cement was added to the synthetic pore solution at a mass ratio of 1:20, and the resulting solution was tumbled for 100 h. Solution samples were
taken at 1, 3, and 7 days of exposure, filtered (using 0.2 μm polypropylene membrane filter) and tested using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) to measure the concentrations of various elements. The chemistry and mineralogy experiments were not duplicated.

3.3.3. Pozzolanic Reactivity

The strength activity index (SAI) of the two fly ashes were measured according to ASTM C311-17 and after 7, 28, and 56 days of curing in a lime water bath. The control mortar mixture was prepared with w/cm=0.484 and sand/cement=2.75 by mass, using type I/II Portland cement (Table 3-5) and standard sand with absorption capacity of 0.58%. In the test mixtures, 20% of the mass of cement was replaced with the anthracite or bituminous CFBC fly ash, and enough water was added to reach a flow ± 5% of the control mortar (measured according to ASTM C1437-15). This resulted in a net increase of the w/cm to 0.53 in mortars containing fly ash. To eliminate the effect of the increased w/cm on the compressive strength of mortars, a second series of mortar samples were prepared, where the w/cm was kept constant between the test and control mixtures, and enough superplasticizer (Master Glenium 7620) was added to the test mixtures to maintain a flow of ± 5% of the control mixture. For both the SAI and mortar strength experiments, three cubes were tested at a given age.

In addition, two test methods were adopted for measuring the pozzolanic reactivity of fly ash; ASTM C593-06 (Standard Specification for Fly Ash and Other Pozzolans for Use with Lime for Soil Stabilization) and RILEM TC TRM267 (Tests for Reactivity of Supplementary Cementitious Materials). According to ASTM C593-06, lime-fly ash mortars were tested for their compressive strength. The mixture design is provided in Table 3-1, where sufficient water was added to produce an ASTM C1437 flow of 65 to 75 %, using 10 drops of the flow table in 6 seconds. Three 50 mm cube specimens were prepared for strength measurement at each age (7 and 28 days).
After casting, the samples were steam cured at 54°C for 7 days, followed by demolding and storing at 23°C and 95%RH until the time of testing.

According to RILEM TC TRM267, lime-fly ash pastes were prepared with proportions provided in Table 3-2, using Ca(OH)₂/pozzolan mass ratio of 3.0, and a water/binder mass ratio of 1.2. Soluble alkalis were added to reproduce the cement pore solution pH and accelerate the pozzolanic reaction, while potassium sulfate and calcium carbonate were added to promote the formation of AFt (ettringite) and AFm phases. The pastes were hand mixed, poured into cylindrical molds (25.4 mm diameter and 20 mm height), sealed, and cured at 40°C to accelerate the pozzolanic reaction. After 1, 7, and 28 days, samples were demolded and ground using a mortar and pestle. To stop the hydration reactions, ground samples were immersed in 100 mL isopropanol for 15 min. The suspension was stirred and poured over a Büchner filter. The residue was dried in a ventilated oven at 40°C for 8 min. TGA testing was conducted by heating the resulting samples from 30°C to 950°C, at the rate of 10°C /min. The TGA chamber was purged with N₂. The unreacted Ca(OH)₂ content of each sample was calculated by measuring the mass loss in the temperature range 375°C to 480°C using the tangent method proposed by Kim and Olek [6], and correcting the results based on an estimated mass of carbonated Ca(OH)₂. The reported results (Figure 3-6) correspond to the testing of one sample per fly ash at a given age. In addition, RILEM TC TRM267 suggests measuring the bound water of the paste at 7 days using the “oven method”. According to this procedure, paste samples were ground using a mortar and pestle, and dried in an oven at 105°C to constant mass. Next, samples were calcined at 350°C for 2 hours, and the mass loss between 105°C
and 350°C was measured and attributed to the loss of bound water. Two samples were tested per fly ash and the average of the two results are reported.

Table 3-2. Lime-fly ash paste mixture design according to RILEM TC TRM267

<table>
<thead>
<tr>
<th>Components</th>
<th>Fly ash</th>
<th>Ca(OH)₂*</th>
<th>Deionized water</th>
<th>KOH#</th>
<th>K₂SO₄#</th>
<th>CaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (g)</td>
<td>11.11</td>
<td>33.33</td>
<td>60</td>
<td>0.24</td>
<td>1.2</td>
<td>5.56</td>
</tr>
</tbody>
</table>

* Contained less than 5 wt.% CaCO₃
# The mixture of KOH and K₂SO₄ was equivalent to 0.3M K

3.3.4. Performance of CFBC Fly Ash in Mortar and Concrete

The performance of CFBC fly ashes in concrete mixtures was evaluated by measuring the fresh properties, including slump (ASTM C143-15a), and fresh air content (ASTM C231-17a). Also, the hardened properties of concrete mixtures were measured, including the compressive strength at 7, 28, and 56 days (ASTM C39-18), and hardened air structure (ASTM C457-16). In addition, setting time (ASTM C403-16), autogenous expansion/shrinkage (ASTM C1698-09), and ASR mitigation efficiency (ASTM C1567-13) was measured using equivalent mortar mixtures. These results were used along with the fly ash characterization results to identify the positive and negative effects of CFBC fly ashes on concrete properties, and to suggest appropriate fly ash beneficiation techniques.

Concrete mixtures were designed using proportions that are typically used for pavement applications in Pennsylvanian. They were prepared with a w/cm=0.47 using type I/II Portland cement (Table 3-5), natural sand (SSD specific gravity of 2.62, absorption capacity of 1.66%, fineness modulus of 2.94), #57 crushed stone (SSD specific gravity of 2.70, absorption capacity of 0.44%, dry rodded unit weight of 1476.4 kg/m³) and water reducing (Master Glenium 7620 by BASF) and air-entraining (MasterAir AE90 by BASF) admixtures. All aggregates met ASTM C33-18 requirements. The concrete mixtures were designed for a slump of 10±2.5 cm (4±1 in.) and air content of 6±1% by volume. Table 3-3 provides the concrete mixture proportions. In the test mixtures, 20% of the Portland cement was replaced with the anthracite or bituminous CFBC fly ash. Two sets of fly ash concrete mixtures were prepared. The first set contained the same AEA
and water reducing admixture (WRA) dosage as that of the control mixture. Generally, these test mixtures resulted in lower slump and lower air content as described later. In the second set, the AEA and WRA dosages were varied to achieve the target slump (10±2.5 cm) and target air content (6±1%) in the fly ash mixtures. For each of the five mixtures, 10 concrete cylinders (diameter of 100 mm and height of 200 mm) were cast and moist cured at 23°C and 100% RH. For each mixture, after 28 days of hydration, a 100×120×10 mm section was cut (perpendicular to the finished surface) from the center of a concrete cylinder, and analyzed for hardened air void distribution. The remaining nine samples per mixture were used for compressive strength testing at 7, 28, and 56 days of age. Three samples were tested at each given age.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Cement (kg/m³)</th>
<th>Fly ash (kg/m³)</th>
<th>Water (kg/m³)</th>
<th>Coarse aggregate (kg/m³)</th>
<th>Fine aggregate (kg/m³)</th>
<th>AEA (kg/m³)</th>
<th>WRA (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>362</td>
<td>-</td>
<td>170</td>
<td>1098</td>
<td>643</td>
<td>0.47</td>
<td>0</td>
</tr>
<tr>
<td>Anthracite CFBC, set 1</td>
<td>290</td>
<td>72</td>
<td>170</td>
<td>1098</td>
<td>639</td>
<td>0.47</td>
<td>0</td>
</tr>
<tr>
<td>Bituminous CFBC, set 1</td>
<td>290</td>
<td>72</td>
<td>170</td>
<td>1098</td>
<td>640</td>
<td>0.47</td>
<td>0</td>
</tr>
<tr>
<td>Anthracite CFBC, set 2</td>
<td>290</td>
<td>72</td>
<td>170</td>
<td>1098</td>
<td>639</td>
<td>0.94</td>
<td>1.40</td>
</tr>
<tr>
<td>Bituminous CFBC, set 2</td>
<td>290</td>
<td>72</td>
<td>170</td>
<td>1098</td>
<td>640</td>
<td>0.47</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Equivalent mortar mixtures were prepared with w/cm=0.47 and sand/cm=2.25. In the test mixtures, enough superplasticizer (Master Glenium 7620 by BASF) was added to achieve a flow of the control mix ± 5%. For autogenous shrinkage testing, the freshly made mortar was poured into sealable corrugated plastic tubes (length of 420 mm and outer diameter of 29 mm) and continuously rotated for the first 24 hours at 23°C and 50% RH. For each mixture, four samples were prepared. The length and mass of each sample were recorded at the time of final setting and at ages of 1, 3, 5, 7, 9, 11, 13, and 15 days. This test was conducted to capture both shrinkage and expansion strains that may occur in mixtures containing CFBC fly ash. To investigate the ASR mitigation capacity
of CFBC fly ashes, mortar bars were prepared and tested according to ASTM C1567-13. These mortars contained a borderline moderately-reactive/highly-reactive river sand (class R1/R2 according to ASTM C1778-16) with SSD specific gravity 2.52 and an absorption capacity of 1.49%. The control mixture was prepared with 100% Portland cement as binder. In the test mixtures, 20% or 40% of the cement was replaced with either CFBC fly ashes. A \( w/cm = 0.47 \) was used and no superplasticizer was included in these mixtures. During the experiment, the mass and length change of each mortar bar was measured as a function of time and to the accuracy 0.01g and 0.0025mm. Four replicate prisms were measured.

### 3.4 Results and Discussion

#### 3.4.1 Physical Properties and Unburned Carbon

The results (Table 3-4) show that both the anthracite and bituminous CFBC fly ashes satisfy ASTM C618-19 requirements of moisture content and soundness. The latter suggests that the fly ashes don’t pose a risk of deleterious expansion caused by the hydration of free CaO and/or MgO. Similar results were also obtained by Wu et al. (2014) [7]. Although the fineness of the anthracite fly ash is greater than the maximum allowable limit of 34%, when passed through #140 sieve (105 µm), it complies with the ASTM fineness limit. Laser diffraction testing show that both fly ashes 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) [8]. Furthermore, SEM imaging (Figure 3-1) show that contrary to the spherical shape of PC fly ash, CFBC fly ash particles have sub-angular shape and internal porosity, consistent with the lower combustion temperature of FBC boilers. These may result in higher water requirement and lower workability of concrete.
Table 3-4. Physical properties and unburned carbon content of fly ash

<table>
<thead>
<tr>
<th>Property</th>
<th>Anthracite CFBC</th>
<th>Bituminous CFBC</th>
<th>ASTM C618 limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (%wt)</td>
<td>0.12</td>
<td>0.18</td>
<td>3.0 max.</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.61</td>
<td>2.63</td>
<td>-</td>
</tr>
<tr>
<td>Fineness (% &gt;45µm)</td>
<td>40.0</td>
<td>29.5</td>
<td>34 max.</td>
</tr>
<tr>
<td>LOI (%wt)</td>
<td>6.65</td>
<td>5.21</td>
<td>-</td>
</tr>
<tr>
<td>Carbon (%wt) using Leco/IR</td>
<td>6.26</td>
<td>3.80</td>
<td>-</td>
</tr>
<tr>
<td>Sulfur (%wt) using Leco/IR</td>
<td>1.01</td>
<td>4.64</td>
<td>-</td>
</tr>
<tr>
<td>Particle size D10 (µm)</td>
<td>2.95</td>
<td>3.42</td>
<td>-</td>
</tr>
<tr>
<td>Particle size D50 (µm)</td>
<td>28.7</td>
<td>26.1</td>
<td>-</td>
</tr>
<tr>
<td>Particle size D90 (µm)</td>
<td>128.0</td>
<td>102.5</td>
<td>-</td>
</tr>
<tr>
<td>Soundness (AC exp. %)</td>
<td>-0.02</td>
<td>-0.03</td>
<td>±0.8 max.</td>
</tr>
<tr>
<td>Water requirement (%)</td>
<td>109.5</td>
<td>109.5</td>
<td>105 to 115 max.</td>
</tr>
</tbody>
</table>

Fineness of Anthracite fly ash passed through No. 140 sieve is 27%

Figure 3-1. SEM images of the anthracite (left) and bituminous (right) CFBC fly ash

The main area of concern is the elevated LOI values for both fly ashes, which may cause problems for air entraining concrete. ASTM C618-19 allows a maximum 6.0% LOI for fly ash and 10% LOI for natural pozzolans. However, up to 12.0% LOI for Class F fly ash is allowed if acceptable air entraining performance can be proven. LOI values >3% often increase the required dosage of AEA, and may result in inconsistent air entrainment and strength of concrete. The fresh and hardened air properties of concrete mixtures containing CFBC fly ashes (results presented in Table 3-6) provide a more accurate insight into their effect on producing concrete with reliable air entrainment. The Leco/IR results show an elevated level of carbon in both fly ashes (higher in the anthracite CFBC)
and an elevated sulfur content in the bituminous fly ash, which is in agreement with the high sulfur content of the bituminous coal. It should be noted that both the LOI and the Leco carbon results are indicative of total carbon contents of the fly ashes, which include both the organic (unburned) and inorganic (carbonates) fractions. Only the organic carbon has a significant impact on the adsorption of air entraining admixtures in concrete.

Table 3-5. Oxide composition of cement and fly ash

<table>
<thead>
<tr>
<th>Compound</th>
<th>Portland cement</th>
<th>Anthracite CFBC</th>
<th>Bituminous CFBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>19.41</td>
<td>50.10</td>
<td>37.64</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.61</td>
<td>22.54</td>
<td>16.88</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.82</td>
<td>7.66</td>
<td>9.91</td>
</tr>
<tr>
<td>S+A+F</td>
<td>27.84</td>
<td>80.30</td>
<td>64.43</td>
</tr>
<tr>
<td>CaO</td>
<td>60.78</td>
<td>5.06</td>
<td>15.39</td>
</tr>
<tr>
<td>SO₃</td>
<td>4.00</td>
<td>2.39</td>
<td>9.83</td>
</tr>
<tr>
<td>K₂O</td>
<td>n/a</td>
<td>2.90</td>
<td>2.09</td>
</tr>
<tr>
<td>Na₂O</td>
<td>n/a</td>
<td>0.35</td>
<td>0.24</td>
</tr>
<tr>
<td>Na₂O_{eq}</td>
<td>0.90</td>
<td>2.26</td>
<td>1.62</td>
</tr>
<tr>
<td>TiO₂</td>
<td>n/a</td>
<td>1.34</td>
<td>0.91</td>
</tr>
<tr>
<td>MgO</td>
<td>2.91</td>
<td>0.75</td>
<td>1.29</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>n/a</td>
<td>0.14</td>
<td>0.13</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.69</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Table 3-6. Effect of CFBC fly ash on concrete properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Control</th>
<th>Anthracite CFBC set 1</th>
<th>Bituminous CFBC set 1</th>
<th>Anthracite CFBC set 2</th>
<th>Bituminous CFBC set 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slump, cm (in)</td>
<td>8.5 (3¼)</td>
<td>2.0 (¾)</td>
<td>4.5 (1¼)</td>
<td>12.5 (5)</td>
<td>11.5 (4.5)</td>
</tr>
<tr>
<td>Fresh air content (vol %)</td>
<td>6.0</td>
<td>1.3</td>
<td>1.5</td>
<td>6.8</td>
<td>6.8</td>
</tr>
<tr>
<td>7-day strength* (MPa)</td>
<td>21.5</td>
<td>24.0</td>
<td>25.2</td>
<td>19.8</td>
<td>22.7</td>
</tr>
<tr>
<td>28-day strength* (MPa)</td>
<td>30.3</td>
<td>35.4</td>
<td>35.6</td>
<td>27.7</td>
<td>31.6</td>
</tr>
<tr>
<td>56-day strength* (MPa)</td>
<td>32.0</td>
<td>36.9</td>
<td>37.4</td>
<td>32.6</td>
<td>33.0</td>
</tr>
<tr>
<td>Hardened air content (vol %)</td>
<td>7.2</td>
<td>2.2</td>
<td>3.1</td>
<td>8.5</td>
<td>8.1</td>
</tr>
<tr>
<td>Air spacing factor (mm)</td>
<td>0.17</td>
<td>0.52</td>
<td>0.37</td>
<td>0.13</td>
<td>0.10</td>
</tr>
</tbody>
</table>

* The coefficient of variation of strength measurements was 4.0% based on three 100×200mm concrete cylinders tested for each mixture at a given age.
3.4.2 Bulk Chemistry and Mineralogy

The chemical requirements of ASTM C618-19, limit the sum of oxides SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$ to 50% by mass for Class F and Class C fly ash. Furthermore, fly ashes with CaO contents greater than 18% are classified as Class C fly ash. It can be seen from the XRF results (Table 3-5) that both fly ashes satisfy the requirements for Class F fly ash. The bituminous coal has higher sulfur content, which requires a larger proportion of limestone to be added to CFBC boiler to capture SO$_x$ emissions. This leads to a higher CaO content of the resulting fly ash.

Both fly ashes show CaO<18% and Na$_2$O$_{eq}$<3.0, suggesting that they may be suitable for mitigating ASR according to ASTM C1778-16. This is later verified using ASTM C1567 testing. To ensure volumetric stability, and in addition to the soundness criteria, ASTM C618 limits the SO$_3$ content of fly ash to 5%. While the anthracite fly ash meets this criteria, the bituminous CFBC fly ash contains 9.83% SO$_3$ (per XRF) and 11.6% SO$_3$ (per Leco/IR); this may result in a deleterious expansion due to ettringite formation. This risk is further evaluated using the autogenous shrinkage/expansion results presented below.

The XRD patterns and Rietveld quantification results are presented in Figure 3-2 and Figure 3-3. Both fly ashes show amorphous contents close to ~50%; this is smaller than the typical glass content of PC fly ash (>75% [4]). This was anticipated given the lower combustion temperature of FBC boilers (<900°C) versus the conventional PC boilers (<1750°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 the anthracite fly ash, and 78.5% for the bituminous 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 (Table 3-5). Previous
literature have also reported quartz, anhydrite, free lime or calcite as the main phases detected in FBC fly ash [9], [10], [11], [12], [13].

Figure 3-2. Quantitative XRD of the anthracite fly ash

Figure 3-3. Quantitative XRD of the bituminous fly ash
The batch leaching results are provided in Figure 3-4, and lead to the following observations: (1) Both fly ashes bind Ca out of the solution, as a result of pozzolanic reaction and possibly formation of AFt and AFm phases. The anthracite fly ash removes Ca faster, which agrees with its lower CaO content. (2) Both fly ashes remove a considerable quantity of alkalis from the solution, even in the absence of solid portlandite to allow a significant degree of pozzolanic reaction. This feature can be beneficial in mitigating ASR. (3) The anthracite fly ash is a significant source of Al, likely originating from the clay phases. The bituminous fly ash is also a source of Al, but to a lesser degree. The soluble Al content of the fly ashes can provide ASR mitigation benefits [14] and can also promote formation of C-A-S-H, AFt, and AFm phases. (4) Silicon concentrations (not shown) exhibited a similar trend as Al, with the anthracite fly ash releasing up to 185ppm Si by 7 days, followed by the bituminous fly ash and the Portland cement, showing [Si]=27ppm and 5.7ppm at 7 days, respectively. (5) The bituminous fly ash release a significant concentration of S into the solution, in agreement with its high SO\textsubscript{3} and anhydrite contents. This may increase the risk of volumetric instability as a result of ettringite formation. The sulfur contents in Figure 3-4d decline over time, potentially due to precipitation of sulfur-bearing AFt and AFm phases.

3.4.3 Pozzolanic Reactivity

The water requirement of both fly ashes was measured as 109.5% (Table 3-4). This is larger than ASTM C618-19 limit for PC fly ash (105%), but smaller than the limit for natural pozzolans (115%). The elevated water requirement is in agreement with the sub-angular shape and the internal porosity of CFBC fly ashes (Figure 3-1).

The strength activity index (SAI) of the two fly ashes are shown in Figure 3-5. The results at 7, 28, and 56 days of age are within the range 86% to 104%, which meet the ASTM C618 minimum requirement of 75%. The anthracite fly ash shows a slightly higher SAI than the bituminous fly ash. It is interesting to note a declining trend in the SAI results with age. It should
also be noted that due to their 109.5% water requirement, the fly ash SAI mortars had a higher w/cm (=0.53) in comparison with the control mortar (100% cement) having w/cm=0.484. This higher w/cm puts the fly ash mortars at a disadvantage with respect to strength development and results in lowering their SAI values. Literature on SAI confirms that FBC fly ash can comply with the requirements of Class F fly ash [9] [15], and that the higher dosage of water required for FBC mixes adversely affects their strength [16].

Figure 3-4. The batch leaching results showing the concentrations of major elements in synthetic concrete pore solution
Figure 3-5. The strength activity index of CFBC fly ashes and the compressive strength of mortars containing 20% CFBC fly ash as a function of age

To exclude the effect of variable w/cm, a second set of test mortars were prepared at the same w/cm=0.484 of the control mortar and with addition of superplasticizer to maintain a similar flow in the control and test mortars (~88%). The cube compressive strength results of these mortars are also presented in Figure 3-5. The three mixtures generally showed similar strength values at 7, 28, and 56 days. However, mortars containing 20% CFBC fly ash had a slightly better strength than the control at 7 days, but this advantage diminished with age as the control mortar gained better strength over time. This may be due to the use of superplasticizer in the test mortars that gave them a head-start in strength development versus the control mortar that did not contain a superplasticizer.

The results of the lime-pozzolan mortar strength (ASTM C593-06) are reported in Table 3-1. They show a substantially better strength for the mortar containing the bituminous fly ash, and this may be due to a lower w/b or higher reactivity of the bituminous fly ash; e.g., a higher amount
of ettringite may form due to a substantially higher anhydrite content in the bituminous CFBC fly ash. It is interesting to note a slight strength reduction between 7 and 28 days in both mortars, which may indicate that some porosity-forming reactions occur after 7 days. But, it should also be born in mind that the samples were steam cured for the first 7 days at 54°C and afterwards, they were moist cured at 23°C and 95% RH. As such, possible changes in the moisture content of the samples may be responsible for the observed strength retrogression.

The 7-day bound water content of the lime-fly ash pastes per RILEM TC TRM267 method was measured as 0.0234 g (2.34%) and 0.0336 g (3.36%) per gram of dried paste for the anthracite and bituminous fly ashes, respectively. The higher bound water content in the bituminous fly ash may indicate a greater reactivity, but this may be primarily a result of ettringite formation due to the larger SO₃ content of this fly ash. The portlandite consumption over time in these pastes was measured by TGA and the results are presented in Figure 3-6. Both fly ashes show similar degree of pozzolanic reactivity at 28 days, with slightly higher Ca(OH)₂ consumption by the anthracite fly ash at 1 and 7 days. At 28 days, each fly ash consumed 0.74 g Ca(OH)₂ per gram fly ash. Increasing the amount of FBC fly ash has been shown in the literature to increase the Ca(OH)₂ consumption due to a pozzolanic reaction. Glinicki et al. [10] reported a reduction in Ca(OH)₂ content from 1.2% to 0.4% by mass after increasing the FBC fly ash replacement level from 20% to 40%.

3.4.4 Performance of CFBC Fly Ash in Mortar and Concrete

Table 3-6 shows the fresh and hardened properties of concretes containing 20% CFBC fly ash and compares these with the properties of the control (100% cement) mixture. Set 1 fly ash mixtures had the same AEA dosage as the control and had no WRA. In these mixtures, the replacement of Portland cement with CFBC fly ash resulted in a reduction of slump and fresh and hardened air content of concrete. The air content reduction can be linked to the elevated LOI of the fly ashes; the anthracite fly ash had a higher LOI and resulted in a lower air content. This indicates that LOI
reduction of these fly ashes may be beneficial for their practical application. The slump reduction is likely due to joint effects of elevated LOI and water demand of CFBC fly ashes. On the other hand, the 7, 28, and 56-day compressive strengths of set 1 mixtures containing CFBC fly ash were greater than the control by approximately 18%. Most of this strength improvement is likely attributed to the lower air content of the fly ash mixtures. According to the literature, each percentage point of additional air content results on average in approximately 5.5% loss of compressive strength [17] [18].

Set 2 concrete mixtures containing 20% CFBC fly ash were prepared by adding sufficient dosages of WRA and AEA to achieve a similar/target slump and air content 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 having a slightly (~1%) air content in the fly ash mixtures. The hardened air void spacing factor for the control and set 2 fly ash concretes was less than 0.203 mm which is maximum allowable limit 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.

The autogenous shrinkage/expansion results (Figure 3-7) show a small (<60 µε) initial expansion at 1 day for the control and the anthracite fly ash mortars. The mortar containing the bituminous fly ash, however, exhibits a larger expansion, up to 247 µε at 3 days. This is likely due to early-age ettringite formation in this mixture. All three mortars subsequently shrank as a result of chemical shrinkage. This autogenous shrinkage was slightly larger in mortars containing CFBC fly ash. Throughout this test, the magnitude of expansion and contraction remained below the tensile strain capacity of concrete (~400 µε). This may suggest that the higher SO₃ content in the bituminous CFBC fly ash does not pose a serious risk of volumetric instability. If anything, the bituminous fly ash acts as a shrinkage compensating additive. Although these results are promising, it is advisable to monitor the volume stability of mortar or concrete containing CFBC fly ash over
a long term and in exposure to moisture, e.g., via ASTM C1038 test, to more confidently rule out the risk of volume instability.

Figure 3-6. Calcium hydroxide content of lime-fly ash pastes per RILEM TC TRM 267 method

The accelerated mortar bar test (ASTM C1567) ASR results are shown in Figure 3-8. All mortars contained a borderline moderately/highly reactive aggregate (R1/R2). Replacement of 20% cement with CFBC 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 anthracite and bituminous fly ashes, respectively. However, these expansions are still above the ASTM failure threshold of 0.1%. The use of 30% anthracite fly ash and 40% bituminous fly ash 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$_2$O$_3$ contents in comparison with the bituminous fly ash. Longer term ASR testing (e.g., ASTM C1293) is recommended.
Figure 3-7. Autogenous shrinkage of mortar samples (zeroed at the time of final setting)

Figure 3-8. ASR induced expansion of mortar samples in ASTM C1567 test
3.5 Conclusions

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

- According to XRD, the two CFBC 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 of the fly ashes. The presence of anhydrite is a notable difference with conventional fly ashes, and is a result of internal SO\(_2\) scrubbing in FBC boilers via injection of pulverized limestone.

- Both CFBC fly ashes met the physical and chemical requirements of ASTM C618-19, except for a borderline high LOI in both fly ashes and high SO\(_3\)% in the bituminous fly ash. The high SO\(_3\) content did not produce a deleterious volume instability during an autogenous expansion test.

- The CFBC fly ashes exhibited good reactivity and strength development in mortar and concrete with a strength activity index of 86% or better at 7 days and 93% or better at 28 days. The compressive strength of mortars and concrete containing 20% CFBC fly ash was similar to the control mixtures at 7, 28, and 56 days.

- Concrete mixtures containing 20% CFBC fly ash and with proper dosing of water reducing and air entraining admixtures could achieve desirable slump and fresh and hardened air contents. These mixtures produced a similar compressive strength to that of the control mixture as early as 7 days of age.
• Both fly ashes could mitigate ASR, with the anthracite fly ash being more effective due to its lower CaO and higher Al₂O₃ and SiO₂ contents.

• Overall, these fly ashes may be used as a beneficial pozzolan in concrete mixtures in their present form. LOI reduction may be considered as a worthwhile beneficiation. Further research is needed to evaluate the consistency of the FBC fly ash properties from a given resource, to identify the reaction products of FBC fly ash in concrete, and to assess the impact of such fly ashes on other properties and durability of concrete mixtures.

3.6 References


Chapter 4

Understanding the Pozzolanic Reaction Mechanism of Fluidized Bed Combustion Fly Ash in Concrete

4.1 Abstract

The low combustion temperatures (750°C to 900°C) of fluidized bed boilers yields fly ashes with an entirely different mineralogical and morphological properties compared to conventional pulverized coal fly ashes. Unlike the high quantities of glassy components in PC fly ash, alumino-silicate bearing phases in FBC fly ash are mainly de-hydroxylated. As a result, interaction of various phases in FBC fly ash with the hydrating cement paste may differ significantly from that of PC fly ash. To understand and characterize the hydration mechanism of FBC fly ash, in this study, binary paste mixtures incorporating circulating bed combustion fly ashes with distinct compositions were monitored for their bulk chemistry and mineralogy over a course of 90 days using XRD and SEM/EDS techniques. Supplementary thermogravimetric analysis and batch leaching tests were also conducted, to quantify the pozzolanic reactivity of CFBC fly ashes and determine the dissolution rate of their soluble species. The main hydration products of CFBC fly ashes in binary mixtures were found to be AFt (ettringite), CO$_3$-AFm (i.e., hemicarbosaluminate and monocarbo-aluminate), and C-A-S-H phases. Bituminous fly ash showed greater pozzolanic properties, whilst mixtures containing anthracite fly ash produced higher amounts of CO$_3$-AFm.
4.2 Introduction

In the last few decades, circulating fluidized bed combustion has emerged as a viable alternative to pulverized coal combustion. In the CFBC process, particles are suspended in air and continuously recycled back to the boiler, in an attempt to increase residence time and lower combustion temperatures compared to PCC. Although this method significantly affects the structure of ash forming minerals (i.e., dehydroxylated as oppose to the glassy structure of PC fly ash), it is considered as an effective way of burning unconventional solid fuels (e.g., low volatile coal, low-quality waste coal, large fuel particles) that are difficult or impossible to use in pulverized coal combustion. The tendency to use more varied fuel sources in CFBC can also lead to wider variation in ash chemistry, and the coarser fuel feed results in larger ash particles [1]. Additional discrepancies between CFBC and PC fly ash composition arise from the use of limestone as an internal scrubber in CFBC boilers. Depending on the amount of limestone addition, CaO and CaSO₄ contents may be significantly greater for CFBC fly ash, which is equivalent to a lower SiO₂+Al₂O₃+Fe₂O₃ content. Differences in the mineralogical composition and morphology of CFBC fly ash compared to PC fly ash will undoubtedly affect their hydration mechanism in cementitious mixtures. While the self-cementitious property of CFBC fly ash has been the subject of a number of studies, the pozzolanic behavior of CFBC fly ash in binary mixtures is not well understood. To address objective 2, in the present study, two sources of CFBC fly ash that had previously been characterized for their physical and chemical properties (Table 3-4, Table 3-5, Figure 3-2, and Figure 3-3) are used as partial replacement of cement, to investigate their effect on the hydration mechanism of binary mixtures.
4.3 Experimental Procedures

Binary paste mixtures incorporating 20% CFBC fly ash (products of anthracite and bituminous coal combustion) are monitored for their chemical composition and mineralogy after 1, 7, 28, and 90 days of hydration using SEM-EDS and XRD techniques, respectively. The main hydration products are identified and compared with OPC samples (cement properties provided in Table 4-1). Supplementary thermogravimetric analysis and batch leaching testing is also conducted to characterize CFBC fly ashes for their pozzolanic reactivity and dissolution rate of various soluble species.

<table>
<thead>
<tr>
<th>Oxide (wt%)</th>
<th>Method</th>
<th>Portland cement</th>
<th>Anthracite CFBC</th>
<th>Bituminous CFBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td></td>
<td>19.41</td>
<td>50.10</td>
<td>37.64</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td></td>
<td>4.61</td>
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<tr>
<td>Fe₂O₃</td>
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<td>7.66</td>
<td>9.91</td>
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<td>0.24</td>
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<td>0.91</td>
</tr>
<tr>
<td>MgO</td>
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<td>2.91</td>
<td>0.75</td>
<td>1.29</td>
</tr>
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<td>P₂O₅</td>
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<td>0.13</td>
</tr>
<tr>
<td>CO₂</td>
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<td>n/a</td>
</tr>
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</table>

Physical parameters

<table>
<thead>
<tr>
<th>Density (g/cm³)</th>
<th>Method</th>
<th>Portland cement</th>
<th>Anthracite CFBC</th>
<th>Bituminous CFBC</th>
</tr>
</thead>
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<td>-</td>
</tr>
<tr>
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<td>ASTM C311</td>
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<td>6.65</td>
<td>5.21</td>
</tr>
</tbody>
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¹ Fineness of Anthracite fly ash passed through No. 140 sieve is 27%
4.3.1 Batch Leaching of CFBC Fly Ash

To monitor the dissolution rate of soluble species from CFBC fly ash into concrete pore solution, batch leaching tests were carried out. Of special interest was the solubility of silicon and aluminum compounds (e.g. dehydroxylated clays), which can lead to the formation of AFm and AFt phases. Also, sulfur and calcium bearing minerals (e.g., anhydrite and free lime) were of interest due to their potential impact on setting and volume stability of the paste; e.g., due to formation of ettringite. Details on the test procedure can be found in section 3.4.2.

4.3.2 XRD and SEM-EDS Analysis of Binary Paste Mixtures

SEM was conducted on paste samples with w/cm=0.47, using type I/II Portland cement, and 20% replacement of cement with anthracite or bituminous CFBC fly ash. For each mixture, 8 paste cylinders (diameter of 25 mm and height of 25 mm) were cast in sealed containers and cured at 23°C. At various ages of hydration (i.e., 1, 7, 28, and 90 days), two samples from each mixture were demolded and cut into disks of approximately 3mm thickness. One sample was vacuum sealed (to prevent carbonation) and used for XRD testing on the same day, while the other was stored in isopropanol for 7 days, to stop hydration. The disk was later embedded in low-viscosity epoxy (LR white resin from SPI Supplies), dry polished down to 0.25 μm, and carbon coated before imaging. Thermo Scientific™ Q250 Analytical SEM (with tungsten emitter) was used. The device was operated under high vacuum (~10^-4 Pa), accelerating voltage of 15kV and working distance of approximately 10 mm. BSE and EDS detectors enabled imaging and mico-analysis of hydration products in the cement-fly ash mixtures. BSE images (magnification of 800 and spot size of 5 nm) were obtained from 10 random locations on each sample, one of which was further analyzed using the EDS detector (magnification of 1000-2000× and spot size of 7-8 nm), to obtain surface elemental maps. Various points of interest on 28 and 90-day samples were also selected for point elemental analysis.
XRD was performed on paste samples to identify the mineralogy of hydrated phases and monitor their evolution over time. The Malvern Panalytical XPert Pro MPD was used in a θ-θ configuration. To improve particle/phase statistics, the disk samples were placed on a spinner stage rotating at 4 rev/s. The incident X-ray beam was Cu Kα radiation (λ=1.5419 Å) 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 min scan. A PIXcel detector in scanning line mode was used.

4.3.3 Thermogravimetric Analysis of CFBC Fly Ash and Binary Paste Mixtures

To better understand the role of CFBC fly ash in the generation of AFm phases and to determine its pozzolanic reactivity, thermogravimetric analysis was conducted on binary pastes samples (mix design provided in section 4.3.2). Raw CFBC fly ash as well as control paste samples were also tested for comparison. The paste samples were cured in sealed containers at 23°C for 1, 7, and 28 days, after which they were demolded and ground using a mortar and pestle. To stop the hydration reactions, 5 g of ground samples were immersed in 200 mL isopropanol for 15 min. The suspension was stirred and poured over a Büchner filter. The residue was dried in a ventilated oven at 40°C for 8 min. TGA testing was conducted similar to the RILEM TC TRM267 procedure explained in section 3.3.3, with the exception of N2 flow rate of 60 mL/min. Portlandite and calcite contents were determined using the Kim and Olek [2] method, and changes in the amount of AFm phases were monitored over time.
4.4 Results and Discussion

4.4.1. Batch Leaching of CFBC Fly Ash

The batch leaching results are provided in Figure 4-1, and lead to the following observations: (1) Both fly ashes bind Ca out of the solution, as a result of pozzolanic reaction and formation of calcium aluminate phases such as ettringite and AFm. The anthracite fly ash removes Ca faster, which agrees with its lower CaO content. (2) The anthracite fly ash is a significant source of soluble Al and Si, likely originating from the clay phases. The bituminous fly ash is also a source of Al and Si, but to a lesser degree. (3) The bituminous fly ash releases a significant concentration of S into the solution, in agreement with its high SO3 and anhydrite contents. The sulfur contents in Figure 4-1d decline over time, potentially due to precipitation of sulfur-bearing AFt phases. (4) The solubility of anhydrite (source of S) in CFBC fly ash is significantly greater than clay phases (source of Si and Al). For this reason, a continuous increase in the concentration of Si and Al is observed with time, while the rate of S consumption is greater than its release after day 1. (5) Slope of the Al curve for control samples decreases with time, indicating greater solubility of Al in C3A compared to clay minerals.
Figure 4.1. The batch leaching results showing the concentrations of major elements in synthetic concrete pore solution

4.4.2. XRD of Binary Paste Mixtures

XRD patterns of hydrated paste samples are provided in Figure 4-2 and Figure 4-3. The patterns are normalized based on the height of the dominant quartz peak at $2\theta=26.65$. At the age of 1-day, strong portlandite and ettringite peaks are detected for both samples. Free lime is highly reactive with water. In fact, most of the lime is slaked in less than an hour [3] [4], with it being completely hydrated within the first couple of hours [4]. The hydration rate of CaO particles are controlled by the surrounding CaSO$_4$ layer. During the desulfurization process, the surface of the CaO particles
react with \( \text{SO}_2 \) (g) and \( \text{O}_2 \) (g) to produce \( \text{CaSO}_4 \), which wraps the particle surfaces [3]. Although this layer hinders reactions, it is heterogenous and the uncoated sections or thinner coated sections may react faster with water [4] [3]. Formation of portlandite increases the pH and promotes the dissolution of active Si and Al in cement and fly ash. Batch leaching results (Figure 4-1b) reveal anthracite CFBC fly ash to be an abundant source of soluble Si and Al. As a result, the hydration of Al in the presence of Ca and S (provided by anhydrite or gypsum) generates ettringite. This coincides with the low amount of aluminate in the diffraction patterns at day 1. Reductions in sulfur concentrations (Figure 4-1d) after 1 day of hydration further confirms the results. Previous studies have reported AFt peaks as early as 30 min [3], and the presence of \( \text{CaCO}_3 \) has been shown to accelerate ettringite formation [5]. Since bituminous CFBC contains higher amounts of CaO and \( \text{SO}_3 \), the intensity of its ettringite and portlandite peaks, relative to its quartz peak, is greater than that of anthracite CFBC.

With the progress of hydration, the amount of alite and belite drop significantly, which is a good indication of C-S-H production during this time. The intensity of ettringite peaks remain relatively unchanged, due to the availability of \( \text{CaCO}_3 \) (source of carbonates) in the mixture. When S is consumed prior to Al consumption, ettringite becomes unstable and converts to monosulfoaluminate (C\(_4\)ASH\(_{12}\), SO\(_4\)-AFm) [6]. However, this conversion may be delayed or stopped when large amounts of carbonates are present in the hydrated paste, as in this case [7]. When FBC fly ash contains very high amounts of S, a continuous increase in ettringite is expected [4], [8], [9], [3]. XRD diffraction patterns show no visible change in the portlandite peak intensities.
Figure 4-2. XRD of the cement paste containing anthracite fly ash

Figure 4-3. XRD of the cement paste containing bituminous fly ash
At later ages of hydration, when S is depleted, CaCO$_3$ reacts with the remaining Al from C$_3$A and calcined clay sources to generate hemicarboaluminate ($C_4A\overline{C}_0.5H_{12}$) and monocarboaluminate ($C_4A\overline{H}H_{11}$). Portlandite is also consumed during the formation of hemicarboaluminate [10]:

\[ C_3A + C\overline{C} + 11H \rightarrow C_4A\overline{C}H_{11} \]  
\[ Eq. (4-1) \]

\[ C_3A + 0.5C\overline{C} + 0.5CH + 11.5H \rightarrow C_4A\overline{C}0.5H_{12} \]  
\[ Eq. (4-2) \]

In the presence of CaCO$_3$, the formation of CO$_3$-AFm is thermodynamically more favorable compared to the formation of monosulfoaluminate [11][12]. While the ettringite in OPC and limestone free mixtures is known to react with C$_3$A to produce monosulfoaluminate, when sufficient amounts of CaCO$_3$ are available ettringite does not decompose [10]. Strong hemicarboaluminate peaks are detected in both fly ash mixtures as early as 7-days, with monocarboaluminate being formed at later ages (detected in 28-days samples). This is due to the lower content of CaCO$_3$ in hemicarboaluminate and its subsequently faster reaction kinetics compared to monocarboaluminate [13]. Studies on the hydration of ternary blends composed of calcium aluminate cement, calcium sulfate hemihydrate and limestone show a similar trend [12]. Finally, the intensity of the CO$_3$-AFm phases are greater for anthracite CFBC paste samples, as they contain greater amounts of soluble Al (Figure 4-1b).

In general, hydration products of CFBC fly ash seem to be similar to LC3 cements, which contain variable amounts of Portland cement, limestone and calcined clay (e.g., metakaolin). Limestone acts as a source of calcite, while calcined clays and Portland cement provide the necessary aluminates for the formation of carboaluminate hydrates [14][15] [16]. XRD results of paste mixtures containing 15% limestone and 30% metakaolin show significant amounts of hemicarboaluminate and to a lesser extent monocarboaluminate as early as 1 day [14]. Since CO$_3$-AFm phases are unstable compounds in sulfate and chloride environments [16], the performance of concrete and mortar mixtures containing CFBC fly ash against sulfur and chloride ion ingress has been evaluated and the results are provided in chapter 4.
The hydration mechanism of blended cement-fly ash mixtures is somewhat different from that of pure Portland cement. Szeles et al. (2019) [17] prepared paste samples using type I/II Portland cement with \( w/cm \) of 0.5, and monitored their hydration over a course of 3 months (10 min, 3h, 21h, 54h, 7 days, and 3 months). Results showed an increase in ettringite peaks up to 54h, after which a decline was observed. Visible portlandite peaks were detected after 24h, and intensified over time. After 3 months of hydration, hemicarboaluminate peaks were also observed. The combined XRD diffraction patterns of 7-day control and CFBC paste samples are provided in Figure 4-4.

![XRD of cement paste containing anthracite and bituminous fly ash after 7-days of hydration compared to control samples](image)

**Figure 4-4.** XRD of cement paste containing anthracite and bituminous fly ash after 7-days of hydration compared to control samples

### 4.4.3. SEM-EDS of Binary Paste Mixtures

To validate XRD results and identify the composition of amorphous phases, BSE images were taken from 10 random locations per paste sample, one of which was chosen for EDS X-ray mapping and the other for EDS point elemental analysis. The Ca, Si, Al, O, K, Mg, Na, S, and Fe elemental maps obtained from EDS X-ray mapping were deemed sufficient for identifying the main mineral...
phases present in each sample. An example of these maps for 90-day paste samples containing anthracite CFBC fly ash has been provided in Figure 4-5.

![Figure 4-5. EDS elemental maps for anthracite paste samples after 90 days of hydration](image)

After compiling the elemental maps and comparing the results to the composition of minerals detected from X-ray diffraction testing, the following phases were identified: cement particles (a), quartz (b), muscovite (c), hematite (d), portlandite (e), calcium silicate hydrate (f), and brucite/talc/dolomite (g) (Figures 4-6, 4-7, 4-8, 4-9). Since the hydration mechanism of clay particles in FBC fly ash is of special interest, only BSE images containing clay particles were chosen for EDS analysis.
Figure 4-6. Phase identification of anthracite CFBC paste after (top) 1 day and (bottom) 7 days of hydration
Figure 4-7. Phase identification of anthracite CFBC paste after (top) 28 day and (bottom) 90 days of hydration
Figure 4-8. Phase identification of bituminous CFBC paste after (top) 1 day and (bottom) 7 days of hydration
Figure 4-9. Phase identification of bituminous CFBC paste after (top) 28 day and (bottom) 90 days of hydration
After one day of hydration, clusters of portlandite crystals can be seen throughout the microstructure, and to a great extent in the vicinity of clay particles. High magnification (i.e. greater than 1500) imaging also reveals a relatively even distribution of fine needle-like ettringite crystals. Magnesium bearing phases are found in small quantities, in the vicinity of cement particles (periclase) or dispersed within the microstructure (possibly talc from bituminous fly ash). As expected, quartz and hematite particles originating from the fly ash act as inert material, remaining unreacted at all ages. After 7 days, visible signs of inner C-S-H gel can be seen on the rims of cement particles, and increase significantly with the progress of hydration from 7 to 28 days. The matrix phase (groundmass) is mainly composed of Al, Si, and Ca, and can therefore be classified as C-A-S-H. Calcined clays have also been shown to react as a pozzolanic material, consuming portlandite and forming mainly calcium aluminum silicate hydrates [14] [15].

In order to properly identify the composition of major phases, especially that of calcium aluminate silicates, point EDS was conducted on paste samples at the age of 28, and 90 days. The results of point EDS is presented in Figure 4-10 and Table 4-2. Table 4-2 provides the average composition (average of 10 points) and phase category of the various points labeled in Figure 4-10. It can be seen that the clay particles are heterogenous, some parts contain greater amounts of Al (point 5 and 6), while others are highly rich in Si and contain very little Al (point 7 and 8). The very light specs in clay particles contain high levels of Fe or Ti. Rims of some clay particles (point 10 and 11) contain Ca, Al, and Si bearing phases, identified as C-A-S-H. This is not the case for all clays, as some seem to be less reactive than others. portlandite (point 9) is also abundantly formed in the vicinity of clay particles. Similar to the EDS maps, inner C-S-H gel (point 3) has almost completely encapsulated the cement particles at the age of 28 and 90 days. The average atomic ratio of Ca/Si for the inner C-S-H gel is 1.39. The Ca/Si ratio of C-S-H in neat Portland cement varies from approximately 1.2-2.3, with an average of 1.75 [18] [19] [20]. Due to the limited resolution of EDS (1×2 μ), the composition of the thin needles could not be identified correctly.
Although these needles are most likely ettringite, they were shown to be rich in Ca and Si with little Al and S, possibly affected by the surrounding C-A-S-H in the groundmass. Highly rich Mg phases with little Ca can be found as components of anhydrous cement (point 17) and when Ca is also significant, as dolomite (point 18). Finally, non-reactive quartz (point 15) and hematite (point 16) minerals are distributed within the paste.

Figure 4-10. Phase identification using point EDS of (top) anthracite and (bottom) bituminous CFBC paste
correspond to Ca(OH)₂ method described by Avet et al. (2019) (90)

To determine the C

The groundmass is a composite of C-A-S-H, AFt and AFm phases.

To determine the C-A-S-H composition, 200 points of the hydrated areas were sampled from each 90-day specimen. In order to exclude intermixing with other phases present in the microstructure (Figure 4-11), the Al/Ca and Si/Ca atomic ratios of the selected points were plotted similar to the method described by Avet et al. (2019) [21] (Figure 4-12). The (0,0), (0,0.33), and (0,0.5) points correspond to Ca(OH)₂, AFt and AFm phases, respectively.
Both anthracite and bituminous paste samples demonstrate C-A-S-H phases with Si/Ca values predominantly in the range of 0.6-0.8. However, the Al/Ca range for the anthracite sample is slightly broader than the bituminous (0.05-0.25 vs. 0.10-0.20). When comparing these results to 28-day control samples (C-A-S-H composition of approximately Si/Ca= 0.5 and Al/Ca=0.05 [21]), it can be concluded that the partial substitution of cement with CFBC fly ash results in C-A-S-H phases with higher Si and Al contents. The overall greater Al content for the anthracite sample agrees with the higher content of soluble Al in its source fly ash. Figure 4-12 shows greater deviation of points towards areas of high Al/Ca and Si/Ca for the anthracite sample. This may be due to the intermixing of C-A-S-H with traces of raw fly ash, possibly underlying the selected area. Unreacted anthracite and bituminous fly ashes correspond to points (9.24,4.90) and (2.28,1.21) on the scatter plot, respectively. As such, intermixing with raw anthracite fly ash may cause a greater shift of results to areas with higher Al/Ca and Si/Ca, compared to bituminous fly ash.
Figure 4-12. Phase identification of C-A-S-H using point EDS of (top) anthracite and (bottom) bituminous CFBC paste
Previous studies on synthetized C-S-H have also reported an increase in the Al uptake when greater supplies of soluble Al are present in the pore solution [23]. The study by Avet et al. (2019) [21] showed an increase in both Al/Ca and Si/Ca with increasing LC3-50 contents (Figure 4-13). The C-A-S-H composition was defined at the right edge of the cloud of points collected, corresponding to the least amount of intermixing. Wilson et al. (2018) measured Ca/(Si+Al) for four systems with SCMs, and found this value to be less than that of pure C-S-H in OPC mix [24]. Richardson and Groves (1997) [25] established a linear relationship between Al/Ca and Si/Ca for the C-A-S-H composition of Portland cement-slag blends (demonstrated as straight line in Figure 4-14 [19]). This relationship was able to correctly estimate the increase in Si/Ca and Al/Ca with the progress of hydration from 4 weeks to 14 months.

Figure 4-13. C-A-S-H composition for PC and LC3-50 (17.0%), (50.3%) and (95.0%) at 28 days of hydration obtained by SEM-EDS (cloud of points and least intermixed composition) and STEM-EDS [21]
4.4.4. Thermogravimetric Analysis of CFBC Fly Ash and Binary Paste Mixtures

Changes in the weight (%) of dry CFBC fly ash and binary paste samples (combusted at 110°C for 20 min) as a function of temperature (°C) is shown in Figure 4-15 and Figure 4-16. The derivative of weight (%/°C) is also included in the graphs, to correctly identify the decomposition temperature of various phases. The main peaks for binary paste samples occur at 150-170°C, 420-430°C, 670-680°C, 830-850°C, which correspond to the decomposition of AFm, Ca(OH)₂, AFm, and CaCO₃, respectively. A similar pattern is also observed for control mixtures, with the exception of low intensity CaCO₃ peaks occurring at 770-780°C (Figure 4-17). The AFm phases are identified as mono- and hemicarboaluminate, based on earlier TGA testing conducted on pure mono- and hemicarboaluminate (Figure 4-18) [20] [26]. In the absence of CaCO₃, formation of monosulfate is more favorable than CO₃²⁻-AFm, as shown in Figure 4-19 [10].
Figure 4-15. TGA results for pastes samples containing anthracite fly ash (after 1, 7, and 28 days of hydration) compared to as received anthracite fly ash

TGA results show little mass loss (just over 2%) during the combustion of anthracite fly ash, while bituminous fly ash displays three major phase decomposition peaks at approximately 400°C, 630°C, and 910°C. The first peak is most likely due to the conversion of Ca(OH)$_2$ to CaO. As for the remaining two, studies by Wei et al. (2015) [27] have shown that when sufficient amounts of unburned carbon are available, iron oxide is reduced in three stages: Fe$_2$O$_3$ → Fe$_3$O$_4$ at 639°C, Fe$_3$O$_4$ → FeO at 982°C, and FeO → Fe at 1124°C. The slight shift in peak position may related to the type of carbon and its combustibility. For instance, TGA results for anthracite fly ash reveal the
possible development of a mass loss peak at temperatures greater than 940°C. This is because anthracite coal is of the highest rank, containing carbon which is much harder to burn than that in bituminous fly ash.

Figure 4-16. TGA results for pastes samples containing bituminous fly ash (after 1, 7, and 28 days of hydration) compared to as received bituminous fly ash
Figure 4-17. TGA results for control pastes samples (after 1, 7, and 28 days of hydration)

The weight percentage of Ca(OH)$_2$ in dried paste samples is plotted as a function of time (Figure 4-20). The slight reduction in portlandite content for OPC samples from 7 to 28 days is possibly due to the errors associated with sample preparation and TGA testing. In fact, a similar trend has been observed in the study by Poon et al. (2000) [28]. Based on previous studies on OPC mixtures [17], the amount of portlandite content continues to increase with age. In binary paste samples, 20% of the cement is replaced with CFBC fly ashes containing low amounts of CaO. Therefore, the fly ash is deemed pozzolanic if the portlandite content in binary mixtures is less than 80% of
the control. This is not the case for anthracite fly ash, despite its high levels of soluble silica and alumina (Figure 4-1a). However, bituminous fly ash displays slight pozzolanic properties.

Figure 4-18. Decomposition patterns for pure limestone, hemicarboaluminate, and monocarboaluminate [26]

Figure 4-19. Presence of monosulfate in limestone free mixtures [10]
Figure 4-20. Calcium hydroxide content in paste mixtures after 1, 7, and 28 days of hydration

To monitor the changes in AFm content with time, TGA measurements are plotted for the temperature range of 450°C to 850°C (Figure 4-21). Tangent lines are also included, in an attempt to clarify the amount of weight loss due to AFm decomposition. Results show higher amounts of AFm phases for anthracite samples compared to bituminous. This is in accordance with XRD patterns which show greater AFm peak intensities for pastes containing anthracite fly ash. Furthermore, the AFm content increases with hydration time. To confirm these findings, the amount of calcite in paste samples was measured using the tangent method. Bituminous samples contained the greatest amount of calcite and their content decreased from 3.21% at day 1 to 2.01% at day 28. At day 1, the calcite content for control and anthracite samples was 1.26% and 0.32%, respectively, and the peaks became undetectable at later ages.

Based on the changes in Ca(OH)₂ and AFm content with time, it can be concluded that anthracite fly ash is more involved in AFm production, whilst the strength development in bituminous samples is attributed to both its pozzolanic reactions and AFm production. The fewer number of C-A-S-H points collected for anthracite samples using SEM-EDS further confirms this statement.
Figure 4-21. Changes in the amount of AFm phases for binary paste samples (after 1, 7, and 28 days of hydration) compared to the control mixture.
4.5 Conclusions

CFBC fly ash contains reactive anhydrite, free lime, calcined clay, and aluminosilica glass, and its main hydration products in binary paste mixtures were found to be ettringite, CO$_3$-AFm, and C-A-S-H phases:

- Calcined clays and anhydrite are responsible for the formation of ettringite at very early ages. Mixtures containing bituminous fly ash contained greater amounts of ettringite, which agrees with the higher anhydrite content in bituminous fly ash.

- When S is depleted, CaCO$_3$ reacts with the remaining Al from calcined clays to form hemicarboaluminate and monocarboaluminate. X-ray diffraction patterns revealed strong hemicarboaluminate peaks at 7 days. The greater CO$_3$-AFm phases in anthracite samples agrees with the higher soluble Al and Si in the source fly ash.

- C-A-S-H is primarily formed from the reaction between C:$S$ and C:$S$ with portlandite, in the presence of Al (from calcined clays). The secondary C-A-S-H phase production was greater for samples with bituminous fly ash, as thermogravimetric analysis results revealed greater pozzolanic reactivity for bituminous fly ash compared to anthracite fly ash. The Si/Ca and Al/Ca values for C-A-S-H of binary paste mixtures were greater than the control.

4.6 References


Chapter 5

Performance of FBC Fly Ash in Concrete

5.1 Abstract

Past studies have been mainly focused on evaluating the effects of FBC fly ash on the mechanical properties of mortar and concrete. In most cases, the 28-day strength activity index of mortar samples is compared against ASTM C618-19 limits, and very little is done in terms of durability testing. This is because current specifications are prescriptive in nature, and lack sufficient performance-based requirements. In fact, the long-term performance requirements of ASTM C618-19 (i.e., drying shrinkage and resistance to sulfate attack) are optional, and apply only when specifically requested by the purchaser. To address these deficiencies, in this study, the durability of concrete mixtures containing CFBC fly ash was evaluated against water absorption and chloride ion penetration. Equivalent mortars mixtures were also tested for their sulfate attack resistance, drying shrinkage, and amount of volume expansion in water. Results showed that the replacement of Portland cement with 20% CFBC fly ash significantly improved concretes’ resistance to chloride ion attack, and its initial sorptivity was equal or less than that of the OPC mixture. The SO₃ in CFBC fly ash did not cause any deleterious expansion, and the drying shrinkage values were within standard limits. While mortar bars containing anthracite fly ash were able to withstand severe sulfate attack, the use of bituminous fly ash led to premature deterioration.
5.2 Introduction

FBC ash is produced in large quantities in the U.S (14.5 MT based on ACAA’s 2017 annual report), but since it is outside the scope of concrete specifications, it is primarily used for mining applications (14 MT) and waste stabilization/solidification (0.1 MT). This is while approximately 36.8% of PC fly ash is used as replacement for Portland cement in concrete and grout. Considering the decade-long shutdown of pulverized coal powerplants and the strong market demand for good quality fly ash, it is essential to investigate the performance of alternative fly ash sources in concrete. In chapter 3, DOT compliant concrete pavement mixtures containing CFBC fly ash with desirable slump and air content were prepared, and monitored for their strength development. Contrary to studies by Gazdič et al. (2017) [1], Wu et al. (2014) [2], and Robl et al. (2011) [3], samples showed compressive strength values similar to that of the control. Although these results are very promising, additional testing is required to evaluate the effect of FBC fly ash on the durability properties of concrete. In an attempt to complete objective 1 of this research, the long-term performance of concrete and mortar mixtures against water adsorption, drying shrinkage chloride and sulfate ion penetration, is evaluated.

5.3 Experimental Procedures

As-received anthracite (passed No. 140 sieve) and bituminous CFBC fly ashes were incorporated into concrete mixtures with adequate slump and air content, and their effect on the short-term (setting time) and long-term (chloride ion penetration and water sorptivity) properties of concrete was investigated. Equivalent mortar samples were also prepared and tested for their drying shrinkage, resistance to sulfate attack, and volume expansion in water. Concrete performance was
related to microstructural features such as pore size distribution and pore conductivity, using MIP and pore fluid extraction methods.

5.3.1 Performance of CFBC Fly Ash in Mortar and Concrete

The performance of CFBC fly ashes (Table 4-1) in concrete mixtures was further evaluated by measuring concretes’ setting time (ASTM C403-16), rapid chloride ion penetration (ASTM C1202-18), and water sorptivity (ASTM C1585-13). Concrete pavement mixtures were prepared using proportions provided in Table 3-3. In the test mixtures, 20% of the Portland cement was replaced with the anthracite or bituminous fly ash, and enough water reducing and air-entraining admixtures were added to achieve a slump of 10±2.5 cm (4±1 in.) and air content of 6±1% by volume (labeled as Anthracite CFBC set 2 and Bituminous CFBC set 2 in Table 3-3).

For each mixture, 2 concrete cylinders (diameter of 100 mm and height of 200 mm) were cast and moist cured at 23°C and 100% RH for 56 days, to be used for rapid chloride permeability (RCPT), and water sorptivity testing. The remaining fresh concrete was wet-sieved through No. 4 sieve, poured into plastic molds (diameter of 150 mm and height of 150 mm), capped, and monitored for its initial and final setting time at various curing temperatures (14°C, 23°C, and 36°C). The initial and final setting time corresponded to resistance to penetration of 3.5 MPa (500 psi) and 27.6 MPa (4000 psi), respectively. Results are reported as the average of three samples. The setting time of paste mixtures (ASTM C403-16), prepared with normal consistency and 20% replacement of cement with fly ash were also tested for comparative purposes. To eliminate the effect of water content on the setting time, similar paste mixtures with constant w/cm=0.285 were cast and tested.

RCPT was used to monitor the amount of electrical charge passed through 50 mm thick concrete slices, during a 6 h 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 0.3N 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 concrete cylinder, and used to measure the rate of water absorption by capillary suction. Prior to testing, samples were vacuum-saturated (ASTM C1202-18), moist cured (50°C and RH of 80%) for 3 days, and subsequently stored in separate sealable contains 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 their mass gain after 1, 5, 10, 20, 30, 60 min and at specified intervals up to 7 days.

To relate concrete properties to microstructural features such as pore size distribution and pore fluid conductivity, equivalent paste samples (diameter of 20 mm and height of 40 mm) were cast and moist cured (at 23°C and 100% RH) for 56 days. Two replicates were prepared for each mixture. Two small pieces (smaller than 1.5 cm diameter and 2 cm length) were cut from the center of one sample and vacuum dried at room temperature prior to MIP testing, while the other sample was used for pore fluid extraction testing. During MIP testing, mercury was forced into the evacuated sample under increasing pressure, and the volume of mercury intruded was measured as a function of pressure. The critical pore diameter (i.e., the mean size of pore entry ways that allows maximum percolation of mercury throughout the pore system), average pore diameter, threshold diameter (i.e., the minimum diameter of pores that form a continuous network throughout the cement paste), and total porosity were among the parameters obtained from this technique [4]. In most cases, the critical pore diameter can be assumed to be similar to the median pore diameter.

The pore fluid extraction setup was used to apply an axial force (rate of 133 to 178 kN/min) to the paste specimens in a confined space, creating high tri-axial pressures that squeeze out the pore fluid. The solution was filtered with a 0.45-µm polypropylene filter, and ICP-AES was
conducted to measure the concentration of sodium (Na\(^+\)), potassium (K\(^+\)), calcium (Ca\(^{2+}\)), and sulfide (S\(_2^-\)) ion species. Stoichiometry was used to calculate the concentration of sulfates (SO\(_{4}^{2-}\)), while titration with hydrochloric acid (HCl) was used to measure the concentration of hydroxides (OH\(^-\)). The model developed by Snyder et al. (2003) [5] was then used to calculate the electrical resistivity of the pore solution:

\[
\rho_{\text{calc}} = \frac{1}{\Sigma_i z_i c_i \lambda_i} \tag{Eq. 5-1}
\]

\[
\lambda_i = \frac{\lambda_i^0}{1 + G_i I_M^{0.5}} \tag{Eq. 5-2}
\]

\[
I_M = \frac{1}{2} \Sigma_i z^2 c_i \tag{Eq. 5-3}
\]

\(\rho_{\text{calc}}\) = electrical resistivity of the solution in \(\Omega\text{m}\);

\(\lambda_i\) = the equivalent conductivity of a single ionic species in \(\text{cm}^2\text{ S/mol}\);

\(z_i\) = the valence concentration of a single ionic species;

\(c_i\) = the molar concentration of a single ionic species in \(\text{mol/L}\);

\(\lambda_i^0\) = the equivalent conductivity of ionic species at infinite dilution in \(\text{cm}^2\text{ S/mol}\);

\(G_i\) = the empirical conductivity coefficient of a single ionic species in \((\text{mol/L})^{-1/2}\);

\(I_M\) = the ionic strength (molar basis) in \(\text{mol/L}\);

\(i\) = a single ionic species.

The values for \(\lambda_0\) and \(G_i\) are provided in literature [6] [5]. The formation factor, which is a measure of concrete’s transport properties, can be calculated from the ratio of electrical resistivity of concrete \(\left(\rho_b\right)\) to the electrical resistivity of the pore solution \(\left(\rho_0\right)\): \(F = \frac{\rho_b}{\rho_0}\) [6].

Performance of CFBC fly ash in mortar mixtures was evaluated by monitoring its drying shrinkage (ASTM C157-17), resistance to sulfate attack (ASTM C1012-18a), and volume
expansion in water (ASTM C1038−14b). For ASTM C1012-18a testing, mortar mixtures were prepared with w/cm=0.485 and sand/cm=2.75, using type I/II Portland cement and graded standard sand. In the test mixtures, enough water was added to achieve a flow of the control mix ± 5% (Table 5-1). Six mortar prims (25×25×285 mm) and nine cubes (50 mm) were cast and stored over water in a tightly secured container at 35°C. After 24 h, the samples were demolded and cured in lime water until reaching a compressive strength of 20 MPa. Once the required strength was obtained, initial comparator readings were taken and the samples were stored in Na₂SO₄ solution (50 g/L). Specimens were removed 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 to the requirements set by ASTM C618-19.

Table 5-1. Mortar mix proportions for ASTM C1012-18a testing

<table>
<thead>
<tr>
<th>specimen</th>
<th>cement (g)</th>
<th>fly ash (g)</th>
<th>sand (g)</th>
<th>water (g)</th>
<th>SP (g)</th>
<th>flow (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>750</td>
<td>-</td>
<td>2062.5</td>
<td>375</td>
<td>-</td>
<td>88</td>
</tr>
<tr>
<td>Anthracite CFBC</td>
<td>600</td>
<td>150</td>
<td>2062.5</td>
<td>409.5</td>
<td>-</td>
<td>86</td>
</tr>
<tr>
<td>Bituminous CFBC</td>
<td>600</td>
<td>150</td>
<td>2062.5</td>
<td>409.5</td>
<td>-</td>
<td>93</td>
</tr>
</tbody>
</table>

Equivalent mortar mixtures were used for drying shrinkage testing, with the exception of a constant w/cm of 0.485. For each mixture, four prims (25×25×285 mm) were cast and moist cured for 24 h, after which they were demolded and placed in lime water for 6 days. At the age of 7-days, initial comparator readings were taken and the samples were moved to a 50% RH and 23°C environmental chamber for drying. Comparator readings were taken up to a period of 150 days. The 28-day drying shrinkage of samples was compared to ASTM C618-19 limits. It must be noted that the requirements for sulfate resistance and drying shrinkage of mortars are optional, and apply only when specifically requested by the purchaser.

The expansion of mortar bars was measured after 14 days of storage in saturated lime water and compared against the limits of ASTM C1157-17, Standard Performance Specification for Hydraulic Cement. The purpose of this test was to capture any possible deleterious expansion
resulting from the high sulfur content in CFBC fly ashes. Four mortar prisms were cast per mix design, with similar proportions as SAI mixtures (section 3.3.3). Samples were demolded after 24 h of moist curing, and initial gauge readings were taken. Subsequent readings were taken after 14 days of storage in saturated lime solution.

5.4 Results and Discussion

5.4.1 Performance of CFBC Fly Ash in Mortar and Concrete

Results for the setting time of concrete mixtures is provided in Tables 5-2. Replacement of cement with CFBC fly ash has increased the need for superplasticizer, which in turn has delayed the setting time compared to the control mixture. The maximum delay corresponds to mixtures containing bituminous fly ash stored at 14°C, where the final setting time has been increased by as much as 5.5 hours. Anthracite fly ash has also delayed the setting time of concrete, but to a lesser extent. A similar behavior is also exhibited for paste samples with normal consistency (Table 5-3). However, these results may be due to the higher water demand of CFBC fly ashes, since the paste samples incorporating anthracite CFBC fly ash show lower setting time than the control mixture at constant w/cm. As for bituminous fly ash, the high content of anhydrite has had a profound effect on its setting performance. Similar to the effect of gypsum on retarding cement hydration, anhydrate can react with C3A and H2O to generate ettringite, which is a much slower chemical reaction compared to that of C3A and H2O. The initial setting time of cement/CFBC fly ash binary pastes (30% replacement level) was reported to double as the SO3 content of the fly ash was increased from 1.26 to 10.67%. The anhydrite in CFBC ash may even serve as an alternative retarder to gypsum in cement-based materials [7].
Table 5-2. Initial and final setting time of concrete

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial setting time (min)</th>
<th>Final setting time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14°C 23°C 36°C</td>
<td>14°C 23°C 36°C</td>
</tr>
<tr>
<td>Control</td>
<td>420 355 250</td>
<td>560 480 315</td>
</tr>
<tr>
<td>Anthracite CFBC</td>
<td>560 450 290</td>
<td>785 620 370</td>
</tr>
<tr>
<td>Bituminous CFBC</td>
<td>670 545 340</td>
<td>905 700 425</td>
</tr>
</tbody>
</table>

Table 5-3. Initial and final setting time of paste

<table>
<thead>
<tr>
<th>Sample</th>
<th>Normal consistency</th>
<th>Constant w/cm (0.285)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial setting time (min)</td>
<td>Final setting time (min)</td>
</tr>
<tr>
<td>Control</td>
<td>160 300</td>
<td>245 330</td>
</tr>
<tr>
<td>Anthracite CFBC</td>
<td>200 340</td>
<td>140 290</td>
</tr>
<tr>
<td>Bituminous CFBC</td>
<td>240 380</td>
<td>240 365</td>
</tr>
</tbody>
</table>

RCPT results can be found in Table 5-4, which show a significant reduction in the total amount of charge passed through 56-day concrete samples, by partial substitution of cement with CFBC fly ash. Based on ASTM C1202-18, control samples demonstrate ‘moderate’ chloride ion permeability (2000-4000 coulombs), whilst CFBC fly ash samples are classified with ‘low’ permeability (1000-2000 coulombs). Chloride ion penetration in concrete is greatly influenced by the concrete pore structure and the presence of conductive ions such as Na⁺, K⁺, OH⁻, etc. In fact, the conductivity (σₜ) of water saturated cement paste is proportional to the conductivity of the pore fluid (σ₀), total porosity (φ), and pore connectivity (β): σₜ = σ₀φβ [8] [9].

Pore conductivity was calculated based on the concentration of Na⁺, K⁺, Ca²⁺, SO₄²⁻, and OH⁻ using the model developed by Snyder et al. (2003) [5] and the step wise procedure provided by Chang et. al (2018) [6]. Results showed higher pore solution resistivity for mixtures containing CFBC fly ash, due to their lower concentration of Na⁺, K⁺, and OH⁻ compared to the control (Table 5-5, Table 5-6).
Table 5-4. Short and long-term performance of CFBC fly ash in concrete

<table>
<thead>
<tr>
<th>Properties</th>
<th>Control</th>
<th>Anthracite CFBC</th>
<th>Bituminous CFBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slump (mm)</td>
<td>83</td>
<td>127</td>
<td>114</td>
</tr>
<tr>
<td>Fresh air content (vol %)</td>
<td>6.0</td>
<td>6.8</td>
<td>6.8</td>
</tr>
<tr>
<td>Hardened air content (vol %)</td>
<td>7.2</td>
<td>8.5</td>
<td>8.1</td>
</tr>
<tr>
<td>Air spacing factor (mm)</td>
<td>0.17</td>
<td>0.13</td>
<td>0.10</td>
</tr>
<tr>
<td>Compressive strength at 56 days (MPa)</td>
<td>32.0</td>
<td>32.6</td>
<td>33.0</td>
</tr>
<tr>
<td>Chloride ion penetration at 56 days (coulombs)</td>
<td>3035</td>
<td>1289</td>
<td>1684</td>
</tr>
<tr>
<td>Initial sorptivity at 56 days (mm/s0.5)</td>
<td>15.3</td>
<td>15.8</td>
<td>9.2</td>
</tr>
<tr>
<td>Secondary sorptivity at 56 days (mm/s0.5)</td>
<td>7.4</td>
<td>9.1</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Table 5-5. Concentration of ions in the pore solution after 56 days (obtained from ICP-AES)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>K (μg/mL)</th>
<th>Na (μg/mL)</th>
<th>S (μg/mL)</th>
<th>Ca (μg/mL)</th>
<th>Si (μg/mL)</th>
<th>Al (μg/mL)</th>
<th>Fe (μg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>5908</td>
<td>2059</td>
<td>127</td>
<td>91.4</td>
<td>10.7</td>
<td>0.79</td>
<td>2.86</td>
</tr>
<tr>
<td>Anthracite</td>
<td>3744</td>
<td>1368</td>
<td>81.0</td>
<td>32.9</td>
<td>18.2</td>
<td>1.68</td>
<td>0.93</td>
</tr>
<tr>
<td>Bituminous</td>
<td>3833</td>
<td>1315</td>
<td>79.2</td>
<td>71.6</td>
<td>16.7</td>
<td>1.46</td>
<td>1.91</td>
</tr>
</tbody>
</table>

Table 5-6. Calculation of resistivity of pore solution using model developed by Snyder et al. (2003) [5]

<table>
<thead>
<tr>
<th>Specimen</th>
<th>K+ (mol/L)</th>
<th>Na+ (mol/L)</th>
<th>Ca2+ (mol/L)</th>
<th>SO42- (mol/L)</th>
<th>OH- (mol/L)</th>
<th>Resistivity (Ωm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.151</td>
<td>0.090</td>
<td>0.002</td>
<td>0.004</td>
<td>0.252</td>
<td>0.187</td>
</tr>
<tr>
<td>Anthracite</td>
<td>0.096</td>
<td>0.059</td>
<td>0.001</td>
<td>0.003</td>
<td>0.157</td>
<td>0.287</td>
</tr>
<tr>
<td>Bituminous</td>
<td>0.098</td>
<td>0.057</td>
<td>0.002</td>
<td>0.002</td>
<td>0.157</td>
<td>0.287</td>
</tr>
</tbody>
</table>

The conditions of RCPT testing are extremely harsh. For on-site conditions (exposure to deicing salts, seawater, etc.) where the rate of chloride ion ingress is quite slow, the higher amounts of alumina in FBC samples can help prevent corrosion of steel by binding chloride ions out of the pore solution. The main form of binding of the chloride ions is by reaction with C₃A to form calcium chloroaluminate (3CaO.Al₂O₃.CaCl₂.10H₂O), also known as Friedel’s salt. A similar reaction with C₄AF results in calcium chloroferrite (3CaO.Fe₂O₃.CaCl₂.10H₂O) [10]. In such conditions, greater amount of chloride binding is expected for anthracite fly ash, as it contains greater amounts of
aluminum and less sulfur. It has been found that increased sulfate ion concentrations result in slightly lower chloride binding, since sulfate ions react with C₃A to form monosulphate or ettringite [11].

Results for the absorption of water in 56-day concrete samples is provided in Figure 5-2. The 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 C1585-13, the initial rate of water absorption is the slope of the line that best fits (a correlation coefficient of greater than 0.98) the data from 1 min to 6 h. The secondary rate of water absorption is calculated in a similar manner based on the results of 1 to 7 days (Table 5-4). The initial and secondary representative error bars (demonstrated on Table 5-4) were measured by averaging the standard deviation of all data points from 1 min to 6 h and from 1 to 7 days, respectively.

![Figure 5-2. Rate of water absorption in 56-day concrete disks](image)

Results show that the initial sorptivity of anthracite samples is similar to that of the control, while the use of bituminous fly ash has reduced both the initial a secondary rate of water absorption. Since the standard error for secondary sorptivity is quite high and in the same order as the variation
among results, a meaningful interpretation for these results cannot be made. Sorptivity is directly related to pore features such as porosity, pore diameter, and pore connectivity. Of special interest are pores greater than 24 nm (calculated using Kelvin’s equation), as they remain unsaturated at 80% RH (used for pre-conditioning samples). The initial sorptivity data is in accordance with MIP results (Figure 5-3, Table 5-7) which shows lower volume of macropores (> 24 nm) for anthracite and bituminous samples. Use of CFBC fly ash has resulted in a finer pore structure and lower porosity which explains the higher formation factor of samples containing CFBC fly ash.

![Graph showing pore size distribution of paste samples using MIP](image)

**Figure 5-3. Pore size distribution of paste samples using MIP**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Porosity (%)</th>
<th>Avg. pore diameter (nm)</th>
<th>Critical pore diameter (nm)</th>
<th>Threshold pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>27.8</td>
<td>12.4</td>
<td>21.1</td>
<td>36.6</td>
</tr>
<tr>
<td>Anthracite</td>
<td>27.3</td>
<td>11.6</td>
<td>11.0</td>
<td>22.0</td>
</tr>
<tr>
<td>Bituminous</td>
<td>26.3</td>
<td>11.6</td>
<td>11.0</td>
<td>24.7</td>
</tr>
</tbody>
</table>

The average 14-day expansion of mortar bars stored in saturated lime is 0.008, 0.005, 0.024%, for control, anthracite, and bituminous samples, respectively. Bituminous samples slightly surpass the
ASTM C1157-17 limit (0.02%), but it is safe to assume that the use of bituminous fly ash will not lead to deleterious expansion in concrete, especially that 3 out 4 specimens had expansion values within limit. Although these results are promising, it is advisable to monitor the volume stability of mortar or concrete containing CFBC fly ash over a long term and in exposure to moisture, to more confidently rule out the risk of volume instability.

Figure 5-4 shows expansion results for mortar bars stored in Na$_2$SO$_4$ solution. The increase in length of samples containing CFBC fly ash is greater than the control, with the highest values reported for samples with bituminous fly ash, at all ages. This behavior is primarily due to the high amounts of soluble aluminum and sulfur in CFBC fly ashes. Sulfate ions react with certain components of hydrated cement to form ettringite and gypsum that induce expansion. Hydrated calcium aluminate and aluminum rich AFm phases transform to ettringite in the presence of sulfate ions, while gypsum is formed in a reaction between portlandite and sodium sulfate [12][13][14]. The formation of ettringite is much more expansive than gypsum, resulting in increased capillary pressure and cracking in hardened samples [10].

![Figure 5-4. Expansion of mortar prisms in Na$_2$SO$_4$ solution](image-url)
Based on batch leaching results (Figure 3-4), it is clear that the concentration of sulfates is significantly high in the pore solution of samples containing bituminous fly ash, even at 7 days. Results for the expansion of mortar bars stored in water proved that when sufficient moisture is available, these sulfates can react with aluminum bearing phases, and cause considerable volume expansion. This is also the case during the initial weeks of storage of samples in Na₂SO₄ solution. High concentrations of sulfate ions within the sample and storage solution, promote both internal and external sulfate attack. After 8 weeks of exposure, the standard deviation of readings becomes significant, indicating severe microcracking in the samples. From this point on external sulfate attack dominates and deterioration is accelerated.

For on-site conditions, where samples are subjected to cycles of wetting and drying, salt crystallization and their accumulation inside pores will further deteriorate concrete [13]. Furthermore, at temperatures below 15°C and when sufficient amounts of carbonate ions (CO₃²⁻) and calcium silicate are available, sulfate attack will result in the production of thaumasite [13]. In general, the deterioration mechanism of concrete is attributed to the failure of concrete to physical attack (salt crystallization in porous media) and chemical attack (chemical reactions leading to expansive products) [13].

The test criteria set by ASTM C618-19 requires a maximum expansion limit of 0.1% and 0.05% after 6 months of exposure for moderate and severe sulfate resistance, respectively. Therefore, samples containing 20% anthracite fly ash can tolerate severe sulfate attack, while the use of bituminous fly ash should be avoided in concretes exposed to sulfates.

Mortar bars containing bituminous fly ash also show greater drying shrinkage compared to anthracite and control samples (Figure 5-5). 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 show a relatively constant increase in shrinkage with time. The 28-day shrinkage of bituminous samples exceeds the control mixture by 0.017%, which is within ASTM
C618-19 limits (max. 0.03%). The finer capillary pore structure in bituminous mortar is the main reason for this behavior, which has been confirmed by MIP and sorptivity test results.

(a) Drying shrinkage and (b) change in mass of mortar samples

Figure 5-5. (a) Drying shrinkage and (b) change in mass of mortar samples
When concrete is exposed to an environment with relative humidity of less than 100%, water is initially lost in the large capillary pores which has little to no effect on shrinkage. With the progress of drying, water is removed from finer capillary pores (smaller than 50 nm size), which develops internal negative pressure, that leads to the shrinkage of concrete. Continued drying also causes the loss of physically adsorbed water from C–S–H gel [15].

### 5.5 Conclusions

This study evaluated the fresh and long-term properties of concrete and mortar mixtures containing CFBC fly ash. The main findings are as follows:

- Regardless of the use of any superplasticizers, bituminous fly ash significantly retarded the setting time of concrete due to its high anhydrite content. Lower curing temperatures (14°C) further exacerbated this effect. The main cause of delay in the setting of mixtures containing anthracite fly ash was the use of superplasticizer or additional water.
- Use of CFBC fly ash improved concretes’ resistance to chloride ion attack, with anthracite fly ash being more effective in increasing the formation factor.
- The initial rate of water absorption for concrete samples containing CFBC fly ash was equal or less than that of the control, mainly due to their lower volume of macropores (>24 nm).
- Expansion of mortar bars containing bituminous fly ash, exposed to moisture, slightly surpassed ASTM C1038-14b limits. Further long-term testing is required to evaluated the risk of volume instability.
- Drying shrinkage of mortar bars containing bituminous fly ash was the greatest among mixtures, but within ASTM C618-19 limits.
- Use of anthracite fly ash is permitted in concretes exposed to severe sulfate attack, whereas bituminous fly ash can cause premature deterioration even in moderate exposure conditions.
5.6 References


Chapter 6

Performance of Beneficiated FBC Fly Ash in Concrete

6.1 Abstract

CFBC fly ash has displayed good reactivity and strength development in mortar and concrete mixtures. It is also beneficial to mitigating ASR and chloride ion penetration. However, its high levels of unburned carbon content can render the fly ash as unsuitable for on-site applications by interfering with the performance of air-entraining admixtures. In this study, the effectiveness of chemical passivation and carbon burn out methods in neutralizing/reducing the unburned carbon content in CFBC fly ash were investigated, using foam index testing and the measurement of fresh and hardened air content in concrete. Results showed slight reductions in fresh and hardened air content of mixtures containing chemically passivated CFBC fly ash, while carbon burn out was effective in reducing the air-entraining admixture uptake of fly ash. Optimum results were obtained with the combustion of fly ashes at 500°C for 2h.
6.2 Introduction

Counteracting the high unburned carbon content in fly ash with proper dosing of water reducers and air entraining admixtures may be an ideal solution when changes in the LOI of the source fly ash is insignificant. For most CFBC power plants, variations in fuel type and combustion process is inevitable and will lead to inconsistencies in fly ash composition and its unburned carbon content. In such cases, a beneficiation step is necessary to condition the ash so it is of acceptable quality for use in concrete. A number of unburned carbon treatment techniques have been successfully tested (e.g., size separation, froth flotation) and even commercialized (e.g., thermal processing using CBO and STAR techniques; chemical passivation using PACT) for PC fly ash. However, the effectiveness of such techniques for FBC fly ash is unknown. To address objective 3, anthracite and bituminous CFBC fly ashes are treated using the chemical passivation and carbon burn out techniques, and the efficiency of these methods in terms of reducing fly ash interference with AEA performance is assessed.

6.3 Experimental Procedures

Previously in chapter 3, the total carbon content (wt.%) was measured using infrared spectroscopy on as-received CFBC fly ashes. The values were found to be less than LOI, and this difference was especially significant for bituminous fly ash. The total carbon content includes the amount of inorganic carbon that does not interfere with AEA performance in concrete. To exclusively measure the organic carbon, CFBC fly ash was initially treated with 10% nitric acid to dissolve the existing carbonates. Two 150 mg duplicate of each fly ash sample were weighed and placed in separate nickel boat liners. Enough 10% nitric acid was added dropwise to completely remove the inorganic
carbon as CO₂ gas. The samples were then dried on a hotplate (<150°C) and tested using the LECO IR, to determine the remaining carbon content (Figure 6-1).

Two techniques were adopted to modify or remove the unburned carbon in CFBC fly ash so that it does not interfere with the air-entrainment admixtures in concrete: chemical passivation and carbon burn out.

Figure 6-1. Determination of organic carbon content in CFBC fly ash using LECO IR
6.3.1 Chemical Passivation

In the chemical passivation method, PC fly ash is treated with sacrificial surfactants that cover the surface of organic carbon, to prevent them from absorbing the air-entrainment admixture [1]. To determine the effectiveness of chemical passivation for CFBC fly ash, anthracite and bituminous fly ashes were sent for treatment to a building materials company with a reputation of successfully treating over 2.5 million tons of PC fly ash using this method. The treated fly ashes were incorporated into concrete (mix design specified in Table 3-3), and their effect on the slump, fresh air content, hardened air content, and compressive strength of concrete (at 7, 28, and 56 days) was compared to unbeneficiated samples.

6.3.2 Carbon Burn Out (CBO)

In the CBO approach, fly ash is combusted at temperatures above carbon ignition (460°C) and below glass devitrification (700°C), to reduce the unburned carbon content. In this study, CFBC fly ashes were combusted at 500, 550, 600, and 650°C, with a heating rate of 10°C/min and residence time of 2h. LOI and LECO IR testing was conducted on the resulting ash to measure the remaining total unburned carbon content. The performance of the raw and beneficiated fly ashes in terms of air-entraining admixture uptake were also evaluated using foam index testing. Although standards for foam index testing are currently not available, preparations are underway for the ASTM standard entitled ‘New Test Method - Standard Method of Test for Determination of the Air-Entraining Admixture Demand of a Cementitious Mixture’. The draft of this document which is mainly based on the methodology developed by Harris et al. (2008) [2] [3] [4] and Sutter et al. (2013) [5] [6], was used as a guideline for the foam index testing conducted in this research. This fairly quick test can provide insight into the performance of cement/SCM mixtures in terms of their air entrainment properties in concrete, relative to the control mixture. For this purpose, 25 mL of distilled water was added to 8 g of cement and 2 g of CFBC fly ash, in an 8 oz. (237 mL) wide-
mouth glass container. The jar was capped and vigorously agitated for 30 sec (rate of 4 ± 0.5 shakes per second and 225 ± 25 mm displacement of the sample container). One drop of 5% (by volume) AEA solution was added to the slurry using a 50 μL pipette, and the container was shaken for another 10 sec. The lid was removed after 20 sec. If a stable foam (for at least 60 sec) was not observed on the surface of the slurry, another drop was added and the previous steps were repeated (i.e., agitation for 10 sec and addition of AEA solution). The total number of drops, concentration of AEA solution, and volume of each drop was used to calculate the foam index value for each fly ash sample. To achieve the best results, the AEA solution strength was chosen such that a stable foam was achieved by adding 15 ± 5 drops of AEA solution. Since beneficiated CFBC samples required less than 10 drops of 5% AEA solution, 2% and 1% AEA solutions were also tested for treated anthracite and bituminous fly ashes, respectively.

6.4 Results and Discussion

The organic carbon content of CFBC fly ashes is provided in Table 6-1. This value is slightly less than the total carbon content obtained from LECO IR testing, indicating the presence of small amounts of carbonates (e.g., CaCO₃) in the fly ashes. In light of this insignificant difference, the effectiveness of fly ash beneficiation techniques is evaluated based on the total carbon content.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>LOI</th>
<th>Total carbon (wt.%) using LECO IR</th>
<th>Organic carbon (wt.%) using LECO IR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracite CFBC</td>
<td>6.65</td>
<td>6.26</td>
<td>6.05</td>
</tr>
<tr>
<td>Bituminous CFBC</td>
<td>5.21</td>
<td>3.80</td>
<td>3.63</td>
</tr>
</tbody>
</table>

6.4.1 Chemical Passivation

The effect of chemically passivated CFBC fly ashes on the fresh and hardened properties of concrete is provided in Table 6-2 and Figure 6-2.
Table 6-2. Properties of concrete incorporating chemically passivated CFBC fly ash compared to that of as-received fly ash

<table>
<thead>
<tr>
<th>Properties</th>
<th>Control</th>
<th>Anthracite CFBC</th>
<th>Bituminous CFBC</th>
<th>Treated Anthracite CFBC</th>
<th>Treated Bituminous CFBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slump (mm)</td>
<td>83</td>
<td>127</td>
<td>114</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>Fresh air content (vol %)</td>
<td>6.0</td>
<td>6.8</td>
<td>6.8</td>
<td>5.5</td>
<td>6.0</td>
</tr>
<tr>
<td>Hardened air content (vol %)</td>
<td>7.2</td>
<td>8.5</td>
<td>8.1</td>
<td>6.78</td>
<td>6.94</td>
</tr>
<tr>
<td>Air spacing factor (mm)</td>
<td>0.17</td>
<td>0.13</td>
<td>0.10</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>Compressive strength at 56 days (MPa)</td>
<td>32.0</td>
<td>32.6</td>
<td>33.0</td>
<td>37.2</td>
<td>37.4</td>
</tr>
</tbody>
</table>

Figure 6-2. Compressive strength of concrete samples after 7, 28, and 56 days of hydration

Mixtures containing treated fly ash show improved slump and strength development compared to non-beneficiated ones. The higher compressive strength is partially attributed to the lower air content of these mixtures. Surprisingly, the air spacing factor has remained relatively unchanged. The air spacing factor which is generally regarded as the most significant indicator of concrete durability against freezing and thawing, is limited to 0.20 mm (0.008 in.) for moderate exposure conditions. This criterion has been met by all samples. Despite improvements in terms of slump
and compressive strength, the chemical passivation technique has not effectively neutralized the unburned carbon in CFBC fly ash, in order to reduce its interference with AEA performance in concrete.

### 6.4.2 Carbon Burn Out (CBO)

The total carbon content (using LOI and LECO IR testing) and foam index values of raw and treated (combusted at 500°C, 550°C, 600°C, and 650°C for 2h) fly ashes is provided in Table 6-3, and Table 6-4. Information on the number of drops of AEA and total volume of non-diluted AEA (mL) used to obtain a stable foam is included in Table 6-3. Results show that combustion of fly ashes at 500°C has had a profound effect on reducing the unburned carbon content and foam index value. Little change is observed with increasing combustion temperatures.

**Table 6-3.** No of drops of AEA (total volume of AEA in mL) required for raw and treated CFBC fly ashes to obtain stable foam.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Anthracite CFBC</th>
<th>Bituminous CFBC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5% AEA</td>
<td>2% AEA</td>
</tr>
<tr>
<td>raw</td>
<td>20 (0.05)</td>
<td>-</td>
</tr>
<tr>
<td>500°C</td>
<td>5 (0.0125)</td>
<td>11 (0.011)</td>
</tr>
<tr>
<td>550°C</td>
<td>6 (0.015)</td>
<td>14 (0.014)</td>
</tr>
<tr>
<td>600°C</td>
<td>6 (0.015)</td>
<td>16 (0.016)</td>
</tr>
<tr>
<td>650°C</td>
<td>6 (0.015)</td>
<td>16 (0.016)</td>
</tr>
</tbody>
</table>

**Table 6-4.** Comparison between Foam Index results and the amount of unburned carbon from LOI and LECO IR.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Anthracite CFBC**</th>
<th>Bituminous CFBC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AEA (mL)</td>
<td>LOI (%)</td>
</tr>
<tr>
<td>raw</td>
<td>0.05</td>
<td>6.96</td>
</tr>
<tr>
<td>500°C</td>
<td>0.011</td>
<td>3.00</td>
</tr>
<tr>
<td>550°C</td>
<td>0.014</td>
<td>2.44</td>
</tr>
<tr>
<td>600°C</td>
<td>0.016</td>
<td>2.17</td>
</tr>
<tr>
<td>650°C</td>
<td>0.016</td>
<td>1.85</td>
</tr>
</tbody>
</table>

* passed through No. 140 sieve.
Treated fly ashes require less than 10 drops of 5% AEA to reach a stable foam. For example, 3 drops of 5% AEA is used for the solution containing bituminous fly ash combusted at 600°C (Figure 6-3). It is clear that 5% AEA is unable to properly distinguish the performance of various fly ashes. For this reason, foam index testing on treated anthracite and bituminous fly ashes is repeated using 2% and 1% AEA, respectively. The lower concentrations yield a stable foam using 10-20 drops of AEA. The second set of results show that increasing combustion temperatures increases the AEA uptake for anthracite fly ashes, despite reductions in its unburned carbon content. A possible explanation for this behavior might be an increase in the exposed surface area on the fly ash. As for bituminous fly ash, changes in temperature has not had a significant effect on the foam index value and unburned carbon content. The unburned carbon content obtained from LOI and LECO IR testing is plotted as a function of temperature in Figure 6-4. Since the differences in LOI and LECO IR values for anthracite fly ash is mainly attributed to the loss of bound water, combustion of the fly ashes has helped remove the bound water, thus eliminating errors associated with LOI testing. This is not the case for bituminous fly ash, where the discrepancies are possibly affected by the decomposition of calcined clays (among other reactions), rather than the loss of bound water from hydrated lime. That is why combustion temperatures of up to 650°C have not been successful in reducing this gap.

In terms of economy and performance, optimum results were achieved by treating CFBC fly ashes at 500°C for 2 h. Although a residence of 2 h time was sufficient for this study, for industrial scale projects further testing is required to obtain the most efficient residence time.
Figure 6-3. Surface of solution containing bituminous fly ash combusted at 600°C, after adding 1, 2, and 3 drops of 5% AEA using a 0.05 mL pipet.

Figure 6-4. Unburned carbon content (obtained from LOI and LECO testing) in CFBC fly ash as a function of combustion temperature.

6.5 Conclusions

- The chemical passivation technique which is currently commercialized for the treatment of PC fly ash, was not effective on CFBC fly ashes and even led to lower air content in concrete.
compared to non-beneficiated samples. The treated fly ashes did however improve the slump and compressive strength at all ages.

- CFBC fly ashes were combusted at 500°C, 550°C, 600°C, and 650°C for 2h, to reduce their unburned carbon content. Treatment at 500°C significantly improved AEA uptake and little change was observed with the increase of combustion temperatures.

6.6 References


Chapter 7

Summary, Conclusions, and Future Approach

The objective of this study was to determine the feasibility of using CFBC fly ash as concrete pozzolan. If successful, large quantities of widely available fly ash sources can supply the market, and this will allow continued production of cheap, durable, and sustainable concrete of the 21st century. Towards achieving this purpose, two sources of CFBC fly ash were characterized for their physical properties, unburned carbon content, reactivity, bulk chemistry and mineralogy, and compared against the requirements of ASTM C618-19, to identify areas of non-compliance. Next, the fly ashes were used as partial replacement of Portland cement, and their effect on the workability, mechanical properties, and durability (against aggressive agents and environmental conditions) of concrete and mortar mixtures was evaluated. Concrete mixtures were tested for their fresh (slump, fresh air content, setting time at various temperatures) and hardened (hardened air content, compressive strength, chloride ion permeability, water absorption) properties. Equivalent mortar mixtures were also tested for their autogenous shrinkage, drying shrinkage, expansion in water, resistance to sulfate attack and ASR. Concrete performance was related to microstructural features such as pore structure and pore fluid conductivity. Based on the results of the initial part of the study, the efficiency of carbon reduction/neutralization techniques that are commercialized for PC fly ash were investigated for CFBC fly ash. Finally, the interaction of CFBC fly ashes with different components of Portland cement was monitored over time using XRD, SEM-EDS, and thermogravimetric analysis of binary paste mixtures. The project findings will be used to develop guidelines for evaluation, beneficiation and use of FBC fly ashes in concrete. These guidelines will be submitted to ACI Committee 232 for review and potential adoption. They can be expanded in the future by ACI and/or ASTM committees to develop specifications. By producing guidelines
and performance measures, concrete practitioners can distinguish good from bad fly ashes, and they can employ feasible beneficiation techniques to improve the quality of this unconventional fly ash.

### 7.1 Conclusions

The key findings of this research are summarized below:

- CFBC fly ashes were in accordance with the physical and chemical requirements of ASTM C618-19, except for the borderline high LOI in both fly ashes, and the high SO₃ content in bituminous fly ash. However, with proper dosing of chemical admixtures, concrete (20% replacement of Portland cement with CFBC fly ash) with desirable slump, air content, and compressive strength was achieved. The 14-day expansion of mortar bars containing bituminous fly ash, stored in water, slightly surpassed ASTM C1038-14b limits, but the SO₃ content did not cause any deleterious expansion during autogenous shrinkage testing. Further long-term testing is recommended.

- CFBC fly ashes showed good reactivity and strength development in mortar and concrete mixtures. The SAI was at least 86% at 7 days and 93% at 28 days, which is greater than the limit set by ASTM C618-19. The compressive strength of concrete containing 20% CFBC fly ash was also similar to the control mixtures at 7, 28, and 56 days. Unlike conventional PC fly ash, CFBC fly ash were able to contribute to the strength gain of concrete as early as 7 days. The results of lime-pozzolan mortar strength (ASTM C593-06), 7-day bound water content of lime-fly ash pastes (RILEM TC TRM267), and thermogravimetric analysis on paste samples containing 20% CFBC fly ash suggest that bituminous fly ash contains greater pozzolan reactivity compared to anthracite.
• The low combustion temperature (750 to 900°C) of FBC boilers, their diverse fuel supply, and internal desulfurization process, results in a fly ash with a relatively similar chemistry but different mineralogy than the conventional PC fly ash. Chemical analyses of CFBC fly ash showed that the major oxides such as SiO₂, Al₂O₃, and Fe₂O₃ were mainly derived from coal, while most of CaO and SO₃ originated from the capture of SO₂ in the boiler by limestone. The reactive phases identified were calcined clay, aluminosilica glass, anhydrite, free lime which made up 74.5% and 78.5% of the mass of anthracite and bituminous fly ashes, respectively. The non-reactive phases included quartz and hematite. Unlike PC fly ash, FBC fly ash is absent of mullite, but can contain considerable amounts of anhydrite, depending on the sulfur content of source coal and amount of limestone addition. Finally, the FBC fly ash particles are sub-angular in shape and contain internal porosity, which results in higher water demand compared to PC fly ash.

• The main hydration products of CFBC fly ash in binary paste mixtures were found to be ettringite, hemicarboaluminate, monocarboaluminate, and C-A-S-H phases. Bituminous fly ash contributed to greater ettringite and secondary C-A-S-H phase generation compared to anthracite fly ash, due to its greater anhydrite content and pozzolanic reactivity. When sulfur was depleted, the CaCO₃ (from cement) reacted with the remaining aluminum and silicon (from calcined clays and cement) to form hemicarboaluminate and monocarboaluminate. Anthracite fly ash contained greater amounts of soluble aluminum and silicon, which led to greater CO₃-AFm phase production. For mixtures containing CFBC fly ash, the Si/Ca and Al/Ca values for the amorphous C-A-S-H phase was greater than the control.

• Proper dosing of CFBC fly ashes can mitigate ASR and chloride ion penetration, due to their high alumina and silica content. They are also effective in lowering pore solution alkalinity and refining the pore structure. Alumina replaces silica at tetrahedral sites within
the C-S-H creating a negative charge region capable of binding a positively charged alkali ion. Since alkali hydroxides are the main contributor to pore solution conductivity and alkali-silica reactions, their reduced content can increase concrete durability against ASR induced expansion and chloride ion ingress. Mixtures containing CFBC fly ash demonstrated acceptable performance in terms of drying shrinkage, and their rate of initial water absorption was equal or less than the control. While anthracite fly ash did not cause any deleterious expansion for samples stored in water or Na₂SO₄ solution, use of bituminous fly ash should be avoided in sulfate rich environments. Long-term testing for delayed ettringite formation is advised for mixtures containing bituminous fly ash.

- The chemical passivation technique which is currently commercialized for the treatment of PC fly ash, was not effective on CFBC fly ashes and even led to lower air content in concrete compared to non-beneficiated samples. The treated fly ashes did however improve the slump and compressive strength at all ages. The CBO technique was carried out at temperatures of 500°C, 550°C, 600°C, 650°C, and residence time of 2h, to reduce the unburned carbon content in CFBC fly ash. Treatment of CFBC fly ashes at 500°C significantly improved AEA uptake and little change was observed with the increase of combustion temperatures.

### 7.2 Future Directions

This research study was focused on materials characterization, performance testing, carbon neutralization/reduction, and understanding the hydration mechanism of CFBC fly ashes. Based on the obtained results, the following suggestions are presented for future research:
• The use of two CFBC fly ashes with distinct compositions was investigated as concrete pozzolan. CFBC powerplants in Pennsylvania mainly run on anthracite and bituminous waste coal, and although bituminous coal is the most abundant rank of coal found in the United States (about 46% reported in 2017), anthracite coal is relatively rare and available in a small amount in Pennsylvania. It is therefore beneficial to evaluate the performance of FBC fly ashes from other coal sources in concrete, especially fly ash obtained from burning sub-bituminous coal, as it is the second most abundant type of coal in the United States (about 45% reported in 2017) [1]. In general, testing of fly ashes from various CFBC powerplants can help categorize areas of non-compliance in fly ashes based on coal source. The temporal consistency of fly ashes also needs to be assessed. The feed fuel for most CFBC burners is low quality coal, which may cause significant variations in the chemical composition and unburned carbon content of fly ashes collected from the same powerplant at different ages.

• In the event that the temporal consistency is low, addition of chemical admixtures is not an effective method for counteracting the high unburned carbon content in CFBC fly ashes. In this case, beneficiation of CFBC fly ash prior to its use in concrete is required. Combustion of fly ash at 500°C for 2h can dramatically reduce the unburned carbon content; however, more cost-effective approaches such as electrostatic separation need to be investigated. Wet processing technologies (e.g., froth floatation, oil agglomeration) are not advised, as they may affect the composition of fly ash, and the costs associated with drying the fly ash after treatment are relatively high.

• The 14-day expansion in water for mortar bars containing 20% bituminous fly ash slightly surpassed ASTM C1038-14b limits. Therefore, additional long-term testing (e.g., delayed ettringite formation) is recommended to determine the volume stability of this mixture when in contact with moisture. If the SO₃ content in bituminous fly ash proves to be
deleterious, various methods for the management of sulfur need to be carried out. This may include the use of sulfur absorbing materials or the employment of bituminous fly ash as a blend with clinker, where the anhydrite in bituminous fly ash acts as a replacement for the gypsum in cement.

- CFBC fly ash should be compared against ASTM C1709−18, Standard Guide for Evaluation of Alternative Supplementary Cementitious Materials (ASCM) for Use in Concrete. This specification consists of five main stages. The majority of testing specified in the three initial stages has been completed in the current study. As part of the requirement for stage four, the performance of ASCM shall be investigated in a broad range of concrete mixtures, with total cementitious materials content varying from 200 to 400 kg/m³. The test program should also include mixtures with various types of commonly used chemical admixtures (e.g., air entraining agents, water reducers, setting time accelerators and setting time retarders) to determine compatibility. Once all four stages are completed and acceptable performance is demonstrated in laboratory tests, field trials for concrete containing ASCM is carried out. A minimum of three field evaluations, each of at least one year in duration should be performed.

- The possibility of using CFBC fly as raw material for calcium-sulfo-aluminate (CSA) cement production should be investigated. This can be achieved by either matching the chemistry of CSA cement by augmenting CFBC fly ash with necessary additives (e.g., bauxite, limestone, PC fly ash) or using CFBC fly ash as a raw material for the preparation of CSA clinker [2] [3]. CSA cements are increasingly being used in specialized applications for their high early age strength and shrinkage compensation properties. They are mainly composed of CaO (approximately 35-45%), Al₂O₃ (approximately 20-35%), and SO₃ (8-20%) [4] [5] [6] [7] [8], and are valued at roughly twice as much as Portland cement ($200/ton).
7.3 References


VITA

Education

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2017-2019 Graduate Research Assistant, The Pennsylvania State University

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Academic Awards

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Presentations


2018 Evaluating the use of Fluidized Bed Combustion (FBC) as concrete pozzolan. Poster presentation at the 20th Annual Pennsylvania Concrete Conference.

Publications


* Chapters 4 and 5 are currently in preparation for publication and will be submitted soon.