DISSERTATION

HIGH-VOLUME USE OF SELF-CEMENTING SPRAY DRY ABSORBER MATERIAL FOR STRUCTURAL APPLICATIONS

Submitted by

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In partial fulfillment of the requirements

For the Doctor of Philosophy

Colorado State University

Fort Collins, CO

Fall 2009

COLORADO STATE UNIVERSITY

September 9, 2009

WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY CHARLES RILEY ENTITLED HIGH-VOLUME USE OF SELF-CEMENTING SPRAY DRY ABSORBER MATERIAL FOR STRUCTURAL APPLICATIONS BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

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ABSTRACT OF DISSERTATION

HIGH-VOLUME USE OF SELF-CEMENTING SPRAY DRY ABSORBER MATERIAL FOR STRUCTURAL APPLICATIONS

Spray dry absorber (SDA) material, or spray dryer ash, is a byproduct of energy generation by coal combustion and sulfur emissions controls. Like any resource, it ought to be used to its fullest potential offsetting as many of the negative environmental impacts of coal combustion as possible throughout its lifecycle. Its cementitious and pozzolanic properties suggest it be used to augment or replace another energy and emissions intensive product: Portland cement. There is excellent potential for spray dryer ash to be used beneficially in structural applications, which will offset CO_2 emissions due to Portland cement production, divert landfill waste by further utilizing a plentiful coal combustion by-product, and create more durable and sustainable structures. The research into beneficial use applications for SDA material is relatively undeveloped and the material is highly underutilized. This dissertation explored a specific self-cementing spray dryer ash for use as a binder in structural materials. Strength and stiffness properties of hydrated spray dryer ash mortars were improved by chemical activation with Portland cement and reinforcement with polymer fibers from automobile tire recycling. Portland cement at additions of five percent of the cementitious material was found to function effectively as an activating agent for spray dryer ash and had a significant impact on the hardened properties. The recycled polymer fibers improved the ductility and toughness of the material in all cases and increased the compressive strength of weak matrix materials like the pure hydrated ash. The resulting hardened materials

exhibited useful properties that were sufficient to suggest that they be used in structural applications such as concrete, masonry block, or as a hydraulic cement binder. While the long-term performance characteristics remain to be investigated, from an embodied-energy and carbon emissions standpoint the material investigated here is far superior to Portland cement.

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ACKNOWLEDGEMENTS

I would like to thank Dr. Paul Heyliger for his support as I returned to graduate school from industry, for his model instruction in the classroom, and for his encouragement as I worked to finish this document. Despite his dislike for the word mentor, he has been exactly that as I have worked to mature as a learner, teacher, colleague, friend and husband.

I would also like to thank the members of my committee. First, I thank Dr. Rebecca Atadero for her energy and consultation in all matters ash. I thank Dr. John van de Lindt for his helpful comments and real-world approach to problems. I thank Dr. Scott Glick for stepping in at the last minute to fill the position as outside committee member and for contributing his input on issues of life cycle assessment.

I gratefully acknowledge the Colorado Commission on Higher Education (CCHE) for support of this research through Contract Number 07 GAA 00018. The fly ash and recycled tire fibers were provided for this research by the Platte River Power Authority and Jai Tire, respectively. I would like to thank all of the industry contacts who helped me along the way including Jon Little of PRPA and the ACAA staff. I also want to recognize students who assisted with this project including Fredrick Busch and Karthik Rechan.

Finally, I thank my friends and family for providing a foundation of love and for being my cheering squad when days were long and productivity light. As this document was nearing its finish, there was no question in their minds that I would finish it and in fine form. I want to specifically thank my wife, Linda, for the innumerable ash-related conversations. Her willingness to focus on my tasks even while her own were overwhelming her is recognized here and celebrated as one of her greatest aspects. Her selfless offering of time and energy will continue to be an inspiration to me.

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1. Introduction

This dissertation is concerned with the utilization of a very specific self-cementing coal ash material called spray dry absorber (SDA) material (or spray dryer ash) produced at the Rawhide Power Station managed by Platte River Power Authority in northern Colorado. SDA material is a combination of fly ash (the light ash resulting from coal combustion) and products of a semi-dry flue gas desulferization (FGD) process, commonly referred to as scrubbing. Flue gas desulferization is required by the Clean Air Act to combat acid rain. SDA material is sufficiently different from fly ash to be considered a unique material on its own, albeit with a majority of its content and some characteristics shared with fly ash.

While this research is specific in scope, its implications are significant and the problem that this work addresses is as big as the world we inhabit. There is an increasing awareness of detrimental and compounding human impacts on the environment; an understanding that humankind's collective materials extraction, non-renewable (fossil) energy use, waste disposal, and emissions of greenhouse gases, toxics, and particulates are unsustainable. Like the fossil-fuel-based economy on which it is built, the promise of coal combustion by-products is finite and these materials will only be available as long as we have coal to burn. Until this class of materials ceases to be an available resource, we should make the wisest use of it possible, diverting as much as is feasible away from landfills and into useful products and processes. Because SDA material in the United States is so underutilized compared to low-sulfur fly ash and European SDA material, and because research into its beneficial use is so minimal, its continued study is critical.

This work is submitted as a humble attempt to promote greater understanding of this very useful by-product.

The remainder of this introduction will be devoted to framing the research and discussion of SDA material. First, climate change and environmental issues will be discussed as they relate to the built environment (where SDA material is most likely to be used) and energy production (the source of the material). Second, the U.S. energy portfolio and coal utilization will be discussed as this is the reason for and source of the ash that is produced. Third, a short history of cementitious and pozzolanic materials will be given to introduce the current state of the building industry and its use of coal combustion products. Fourth, a description of fly ash and spray dryer ash will be provided. Fifth, the details of the production and use of coal combustion by-products will be outlined with fly ash discussed in general and SDA material discussed specifically. Finally, this background will be used to make the case for the research that was performed.

1.1 Climate Change

Changes in climate due to natural and human activity have the potential to dramatically affect life on earth as it currently exists through more frequent and severe weather phenomena and rising sea levels. Climate change is defined by the Intergovernmental Panel on Climate Change (IPCC) as "a change in the state of the climate that can be identified (e.g. using statistical tests) by changes in the mean and/or the variability of its properties, and that persists for an extended period, typically decades or longer. It refers to any change in climate over time, whether due to natural variability or as a result of human activity" (2007). The IPCC Synthesis Report (2007) states that "Most of the observed increase in global average temperatures since the mid-20th century is *very likely* due to the observed increase in anthropogenic greenhouse gas concentrations." Anthropogenic factors are those that can be adjusted based on human activity and are the focus of IPCC recommendations for mitigation. Fossil fuel burning is the single largest source of greenhouse gas (GHG) emissions, which consist primarily of CO_2. CO_2 is the most plentiful greenhouse gas and the warming potential of all other greenhouse gases is commonly reported in terms of "CO_2 equivalent" or "CO2e," the equivalent amount of CO_2 that would cause the same response as a unit amount of another GHG. Climate change concerns the contents of this dissertation in two ways: 1) the coal ash under investigation is a direct result of coal burning resulting in direct CO_2 emissions and 2) Portland cement, for which the material considered here is a potential alternative, requires significant resource extraction, energy input, and processing with large associated CO_2 emissions. Making greater use of a coal combustion by-product to offset another emissions-heavy product makes good sense from a climate and economic perspective. Additional research is required to accurately characterize the material and develop potential products.

1.2 Energy and Coal

The United States energy portfolio for transportation, industry, buildings, and electricity is made up of fossil, renewable, and nuclear energy sources (Figure 1.1). In 2007, the Energy Information Administration (EIA) reported that the energy produced by coal made up 22.8 percent of the total U.S. energy consumption and that 91 percent of that was used to produce electric power. Coal is the largest source of electricity in the U.S. providing more than half of the electricity used annually.

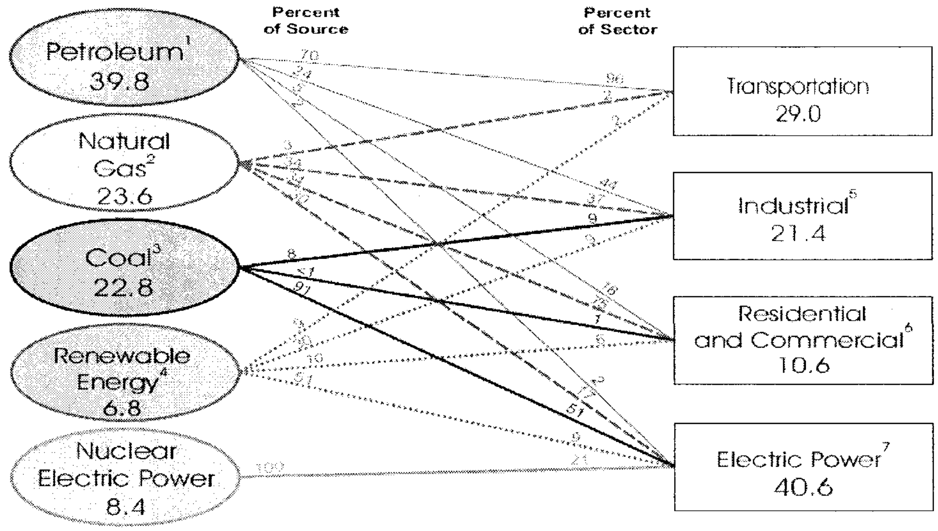


Figure 1.1. U.S. primary energy consumption by source and sector, 2007 (Source: Energy Information Administration).

Both domestic production and use of coal is projected to increase until 2030 if not longer and coal consumption is expected to grow at an annual average rate of 0.6% (EIA, 2009). A significant amount of new resources are projected to come from the Powder River Basin in Montana, Wyoming, and North Dakota, which is the source of the coal precursor to the ash used in this study (EIA, 2009). However, changes in greenhouse gas policy may significantly reduce this number and projections are highly dependent on coal prices. The EIA states that the U.S. uses just over a billion short tons of coal each year and has recently estimated the recoverable coal in the nation's reserves at 263 billion short tons (EIA, 2009b) Thus, recoverable coal reserves are estimated to last approximately 200 years at currently projected growth rates.

The continued use of coal as an energy source will require that the beneficial use and disposal of its byproducts be handled with due consideration of environmental, social, and economic impacts (NETL Trends, nd.). This has myriad implications at power plants where by-products and emissions are increasingly regulated, in the U.S. economy as it seeks a more secure energy future moving away from foreign sources of fuel, and in the world as it struggles to mitigate the negative environmental impacts of coal power plant emissions in the form of particulates, acid gases, and greenhouse gases. The future of coal combustion by-products is inextricably linked to the coal resource. If coal is to be used until it is exhausted, every possible attempt should be made to reduce the quantity and impact of emissions and make beneficial use of every aspect of the resource, including waste heat and combustion by-products.

Based on the 2009 U.S. Greenhouse Gas Inventory Report, greenhouse gas emissions attributed to coal burning for electricity generation make up approximately one third of the U.S. annual emissions (1,967.6 million tonne CO_2E) (EPA, 2009). Such an enormous greenhouse gas output should, with its environmental and climate-related costs, produce a very large amount of utility, which, it can be argued, it does in the form of electricity. However, to have potentially useful coal combustion by-products treated purely as waste as the costs of climate change begin to outweigh the benefits of electricity produced suggests that man use his resources more effectively. While energy efficiency measures can potentially reduce the amount of coal consumed and therefore coal combustion by-products produced, the construction industry has the greatest role to play in making beneficial use of coal combustion by-products in the built environment.

1.3 Concrete, Cement, and the Built Environment

The built environment long ago was blessed with the discovery of quick lime, limestone rock that, once heated and ground, could be mixed with water to produce a very dense and durable hardened product. Lime plaster dates back to 2500 BC in India, Mesopotamia, China, and the Mediterranean and possibly as far back as 7000 BC in Israel (King, 2005; Malinowski, 1991). This precursor to modern concrete required another discovery: reactive silica, the primary component in most pozzolans, including fly ash. Once combined, quicklime and pozzolans produce an extremely hard material that can cure underwater, a product called hydraulic cement. The Romans used this material in their many significant civil engineering works by combining quicklime with the volcanic soils of Pozzuoli, Italy, which is where we derive the term pozzolan (King, 2005).

A pozzolan is “a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious property but which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementing properties” (ASTM C 618). Commonly used pozzolanic materials include volcanic ashes, calcined clays, and fly ash from coal combustion power plants, which can be either pozzolanic or cementitious depending on the amount of calcium it contains (Malhotra and Mehta, 1996). Pozzolans are recognized to improve numerous properties of concrete, particularly long-term strength and durability. Due to the sufficient calcium present in the spray dryer ash used in this study, it is cementitious and pozzolanic rather than simply pozzolanic.

Portland cement, patented in 1824 by Joseph Aspdin, provided man with a material that hydrated and hardened much more quickly than the pozzolanic materials that came before it and, in conjunction with the industrial revolution, ushered in an era of intense development (Sharp, 2006). Portland cement is created by heating properly proportioned feedstock consisting of calcium carbonate (usually from limestone, chalk, marl, or sea shells) and silica, alumina, and iron oxides (which are clay minerals and are incidentally the most commonly occurring oxides in fly ash) to high temperatures in a kiln. During calcination, CO_2 is driven from the raw calcium carbonate to produce so-called clinker, a composition of calcium silicates, calcium aluminates, and calcium aluminoferrites in pebble-sized particles. The clinker is finely ground to produce a highly reactive hydraulic cement and the feedstock may be adjusted to produce the various types of Portland cement that are in common use today. The total CO_2 emitted during Portland cement production results from three distinct processes: (1) the energy required for resource extraction and transportation, (2) the energy required to heat the kiln (2700 ^{o}F) and (3) the calcination of limestone to produce clinker (Mehta and Monteiro, 2006).

The ratio of CO_2 emissions to Portland cement clinker manufacture is nearly one-to-one by mass (Mehta and Monteiro, 2006). This statistic is often misapplied to concrete due to the common and incorrect layman's equivalency of cement and concrete. The amount of CO_2 emitted in the production of Portland cement is significant, but when the product is concrete with its various other inputs, the emissions factor is closer to 0.2. In general, the reduction of Portland cement in a concrete mix will have associated reductions in embodied energy and CO_2 emissions. Any substitution of Portland cement by mineral admixtures such as fly ash yielding a hardened product with equivalent properties has a significant reduction in CO_2. While a full life cycle assessment is beyond the scope of this dissertation, an analysis of expected life cycle benefits of the material investigated here will be provided in the Literature Review and Discussion chapters.

Flower and Sanjayan (2007) note that the only material consumed by humans in greater quantities than concrete is water. Global per capita annual concrete use is reported to be one ton (Lippiatt and Ahmad, 2004; Flower and Sanjayan, 2007), which represents the most consumed construction product in the world on a mass or volume basis. The production of Portland cement contributes five to seven percent of the global CO_2 emissions annually (Sharp, 2006; Mehta, 1999; Huntzinger and Eatmon, 2009). Hence, the potential for improvements in fly ash technology to impact the concrete industry and climate is significant and well-recognized and the contribution to a more sustainable future is widely touted (Malhotra and Mehta, 2008; Kumar et al, 2007; Babbitt, 2008)

The Intergovernmental Panel on Climate Change reported in their 2007 Synthesis Report the potential for efficient buildings to have the greatest impact on anthropogenic CO_2 emissions compared to other economic sectors. While energy efficiency makes up a large portion of this potential CO_2 impact, building materials also represent a significant source for CO_2 savings. CO_2 emissions are reduced through building material selection that utilizes coal-combustion by-products through (1) Portland cement replacement, (2) efficient use of the coal resource to produce building product feedstock as well as electricity, and (3) the creation of more durable buildings with longer design lives.

1.4 Coal Combustion By-Products: Fly Ash and Spray Dry Absorber Material

Coal ash is generally considered to be a waste product or a by-product of coal combustion because the energy produced from coal combustion is the primary product. Coal ash is the mineral residue resulting from the coal combustion process in dry pulverized coal combustion facilities. The components of coal ash are bottom ash, a low-reactivity mineral by-product that falls to the bottom of the combustion chamber and fly ash, a high-reactivity material that is fine enough to travel out of the combustion chamber with the flue gases. The molten ash particles cool as they leave the combustion chamber and form spheres of mostly glassy material (ACAA, 2003). In the early days of coal combustion, fly ash was the particulate emission that provided pictures of smoke stacks spewing soot. It is now collected by mechanical separators and electrostatic precipitators or bag house filters before the flue gases are released. It is subsequently stored or disposed of in landfills and ash ponds or distributed for beneficial use. The type of coal and the combustion, capture, and emissions control processes will dictate the specific physical and chemical characteristics of the ash (ACAA, 2003).

In general, fly ash is composed of solid and hollow spherical particles and broken portions of these ranging between 1 μm and 100 μm in diameter, with an average diameter around 20 μm (Malhotra and Mehta, 1996). Fly ash contains mostly glassy phases with some crystalline phases and may be mixed with unburned coal. This unburned coal is referred to as free carbon and quantified in chemical characterizations as loss on ignition (LOI). Spray dryer ash that is recombined with the fly ash stream consists of fly ash particles coated and mixed with calcium/sulfur reaction products and sorbent (lime) material (EPRI, 2007).

Fly ash for use in concrete is generally classified by ASTM C 618 as either Class C (self-cementing or high-lime ash resulting from combustion of sub-bituminous or lignite coal) or Class F (low-lime ash resulting from combustion of bituminous or anthracite coal). However, fly ash for use in concrete must also adhere to quality standards based on the levels of unburned carbon and sulfur trioxide (ASTM C 618). According to research that will be discussed in more detail in the Literature Review section, materials with excessive levels of these elements may not be appropriate for concrete but may have other low-grade uses.

The fraction of total U.S. coal types by production volume, their primary sources, and the type of fly ash produced is provided in Table 1.1. The carbon content for each is also given with so-called low-rank (i.e. low energy density) coals like lignite having low carbon contents and high-rank (i.e. high energy density) coals like bituminous and anthracite having higher carbon contents.

Table 1.1. U.S. coal types, production fraction, carbon content, primary sources, and resulting fly ash types.

Coal Type	Percent of U.S. Coal	Carbon Content	Main Source in the U.S.	Type of fly ash produced
Lignite	7%	25-35%	Texas, North Dakota	Class C
Sub-bituminous	44%	35-45%	Wyoming	Class C
Bituminous	50%	45-86%	West Virginia, Kentucky, Pennsylvania	Class F
Anthracite	0.50%	86-97%	Northeastern Pennsylvania	Class F

As the technology of coal combustion changes and greater emissions controls are implemented, the constitution of fly ash is changing and new or additional by-products are being produced. Thus, the research of fly ash materials is an ever-changing field of study and the availability of fly ash with a certain quality or composition is not indefinite. For example, as coal power plants have complied with tighter emissions standards, the level of sulfur trioxide in the resulting fly ash has increased. The research conducted here is necessary to determine if the modified material is appropriate for the many uses already identified for fly ash.

At the Rawhide Power Station, SDA material, or spray dryer ash, is produced when a portion of the fly ash from the combustion process is mixed with lime and water to produce a sorbent slurry that is dispersed into the spray dry absorber chamber through a rotary atomizer. This creates a fine mist of sorbent material that reacts with SO_2, SO_3, and hydrogen chloride (HCl) before passing out of the chamber as a dry ash that is recombined with the fly ash stream and collected in the baghouse filters. These filters are periodically cleared and the ash is collected in a storage silo. The vast majority is transported by truck to a monofill on site, while a very small amount is delivered via closed trailer to users in the area.

It should be noted that the combination of SDA discharge and fly ash is a common process in American coal fired power plants. In Europe, fly ash and SDA material are often collected separately. The fly ash is gathered prior to any flue gas desulfurization processes resulting in a less sulfite rich product and allowing for more of both the fly ash and the more sulfite rich SDA material to be used beneficially (Little, personal communication; EPRI, 2007). The product resulting from the Rawhide plant has higher sulfur and calcium contents than traditional Powder River Basin coal fly ashes but is not the pure sulfite SDA material of European plants. Other differences in material properties will be discussed in detail in the Experimentation chapter.

1.5 Fly Ash and Dry FGD Material Production and Use

While fly ash production is relatively steady, its beneficial use increased progressively between 2001 and 2007 according to the American Coal Ash Association (ACAA), which surveys utilities annually to determine coal combustion by-products production and use (Figure 1.2). While fly ash production was around 70 million short tons in 2007, dry flue gas desulferization products, which consist primarily of SDA material, are produced in far smaller quantities: only 1.8 million short tons according to ACAA. Furthermore, the use rates for fly ash and dry FGD materials are very different. Dry FGD production and use between 2002 and 2007 is given in Figure 1.3 for comparison to fly ash production and use in Figure 1.2. In 2007, fly ash beneficial use was reported by ACAA to be 44.1 percent compared to 8.3 percent for dry FGD materials. The dry FGD material use rate reported by ACAA is variable from year to year due to changing respondents to the survey but it is consistently reported to be around ten percent, which is significantly lower than any reported fly ash use rates.

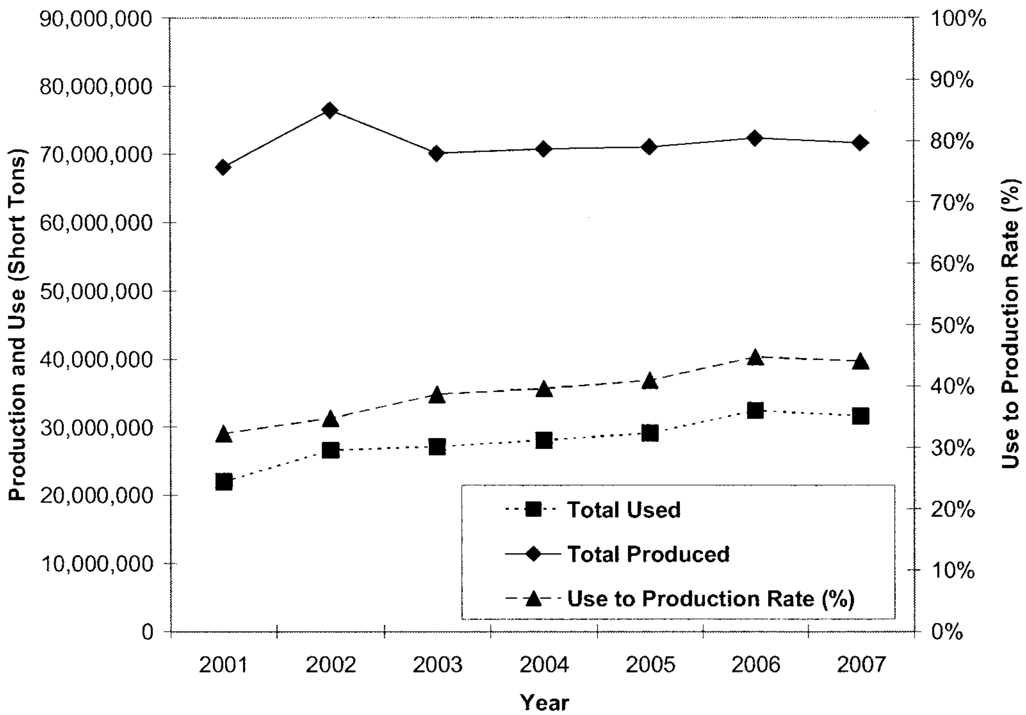


Figure 1.2. Production and use of coal fly ash between 2001 and 2007 (ACAA).

The ACAA survey has response rates around 60 percent and is intended to capture the actual production by utilities. SDA materials are a subset of dry FGD materials and have similar properties, but ACAA has never requested data on SDA materials specifically. The Electric Power Research Institute (EPRI, 2007) has produced estimates specific to SDA materials based on currently installed infrastructure and per-megawatt SDA material production rates. EPRI estimates that between 3.3 and 3.8 million tons of SDA material were produced annually in the U.S in 2007, which is more than the ACAA survey suggests, but is likely a more accurate figure. SDA material production is projected to increase with new installation and retrofit systems on existing power plants with possibly 13 to 14 million tons produced annually by 2017 (EPRI, 2007). Thus, attempts to find beneficial uses for SDA material are important given the future increased production of SDA material as well as the low current use rates.

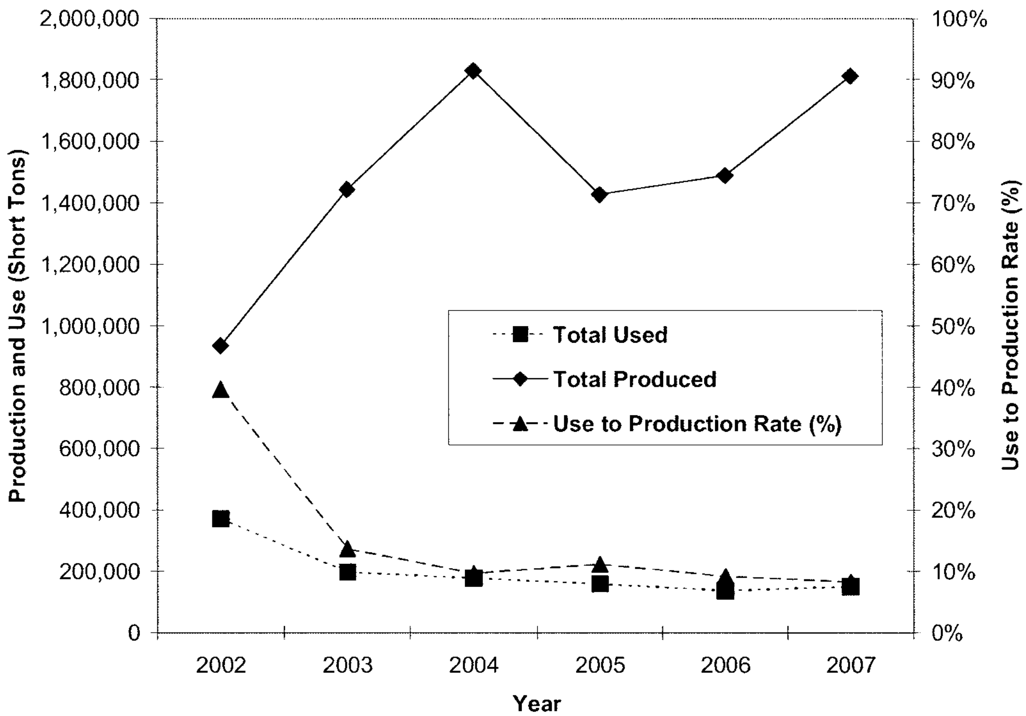


Figure 1.3. Production and use of dry flue gas desulferization (FGD) material between 2002 and 2007 (ACAA).

In 2007, ACAA reported that 8.3 percent of the SDA material produced in the U.S. was used beneficially, with most of it in mining applications. The European Coal Combustion Products Association (ECOBA) reported that in Europe nearly 80 percent is used beneficially (approximately half of that in mining applications) and that multiple countries recently added to the EU have 100-percent utilization rate for SDA material (EPRI, 2007). However, this is likely due to the smaller overall production from these countries and the different material composition of European SDA material compared to the U.S. material (in Europe SDA material is primarily calcium sulfites and sulfates without fly ash mixed in) (Malhotra and Mehta, 1996). Regardless, these statistics indicate that greater beneficial use of SDA material is possible either through increased research or modified material capture methods.

Fly ash has been recognized since the inception of coal burning for electricity as an effective material for a variety of applications beginning with low-value fills and progressing with time to high-value highly researched applications. The applications in which fly ash has been used in some capacity are cement and concrete products, raw kiln feed for cement production, structural fills and embankments, road base materials, flowable fills, mining reclamation operations, waste stabilization and solidification, soil amendments in agriculture, and mineral fillers in asphalt, plastics, metals, paints, and other high-value consumer products (ACAA, 2003). Fly ash can also be used in metal matrix composites and spun into mineral wool at high temperatures for use as a thermal and sound insulation (ACAA, 2003). SDA material has similar potential uses, although with lesser research, concerns about reactions involving sulfates, and the cautious nature of industry to adopt new materials, its use has been limited.

The most recent survey by the ACAA provides the various beneficial use applications to which fly ash and dry FGD material are regularly applied. These are depicted by the proportion of the material produced for fly ash in Figure 1.4 and for dry FGD material in Figure 1.5. Dry FGD material is clearly used in lower-value applications and in far lesser quantities compared to fly ash.

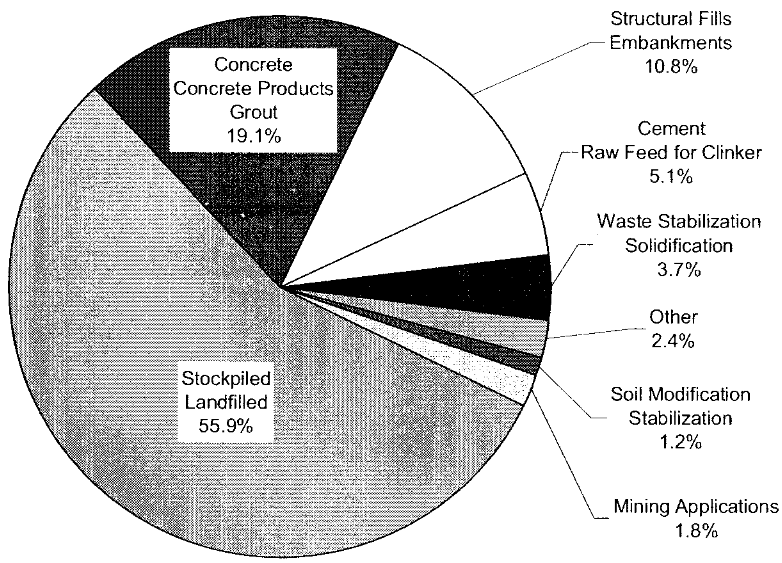


Figure 1.4. Proportion of fly ash used by category in the U.S. in 2007 (ACAA, 2007).

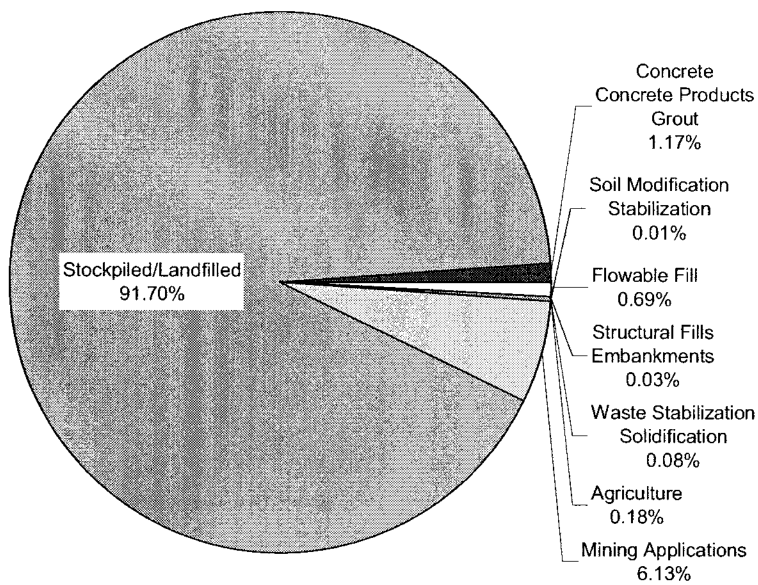


Figure 1.5. Proportion of dry FGD material used by category in the U.S. in 2007 (ACAA, 2007).

A survey by the New Mexico Bureau of Mines and Mineral Resources states:

> "The classification and quality of fly ash can be very important in determining whether fly ash is sold. Fly ash contaminated by FGD by-products is a major factor. Seven of the 38 responding power plants list FGD material collected with some or all of the fly ash as the reason their material is not sold, amounting to 1.44 million metric tonnes of disposed fly ash" (Hoffman, nd.).

The survey refers to the Rawhide Power Station specifically and notes that the spray dryer process serves to "contaminate the fly ash and effectively make this material unusable." The perception that spray dryer ash is not usable is based on limited research and the relatively poorly understood process of sulfate attack that may be mitigated with further investigation. SDA material has a history of being used beneficially in low-value applications like mine reclamation and flowable fill. However, it has also been used with some success in concrete and cement applications. The U.S. Environmental Protection Agency's C^2P^2 Program is calling for 50 percent utilization of CCBs by 2011 with increased beneficial use expected in all categories (Heebink, 2007). Further study of SDA material for structural applications is critical to furthering its use and increasing the low beneficial use rates.

1.6 Objective of the Dissertation

As this introduction has shown, coal combustion by-products have enormous potential to benefit the built environment while offsetting CO_2 emissions, reducing natural resource extraction and diverting landfill waste. However, research in certain aspects of beneficial use is light. Fly ash has been investigated primarily as a cement replacement for structural and non-structural concrete products, as a primary bonding material in controlled low-strength materials, and more tentatively as the sole bonding material in a hardened product for structural applications. The work presented here seeks to use self-cementing SDA material in the latter application. This has the benefit of making use of large quantities of an underutilized form of coal ash that is likely to see increased production in the coming years. Traditional methods of activation and performance improvement are investigated: chemical activation by inclusion of Portland cement and mechanical improvement by inclusion of polymer fibers. The use of polymer fibers from automobile tire recycling further diverts a plentiful waste product from landfills and into a beneficial use. Few studies to date have investigated fly ash from this perspective and none have documented SDA material development, although a number of authors recognize the potential benefits and call for additional research in this area (Naik and Chun, 2003; Kumar, 2007; EPRI, 2007). Some have developed 100-percent fly ash products (Cross et al, 2009; Liu, 2005; Fernandez-Jimenez et al., 2006), but additional work is required for proof of concept and industry acceptance. With the variability of fly ash and SDA material in quality and by region, the content of this dissertation can clarify how spray dryer ash can be used in structural applications and add to the body of knowledge of this very useful industrial by-product.

The objective of the research presented here is to break down the largest barrier to implementation of fly ash in general and spray dryer ash specifically, the perception that it cannot perform on a strength basis with Portland cement based materials when cured under atmospheric temperatures and pressures. This work is intended to accurately characterize the spray dryer ash in question, consider potential mechanisms for the observed strengthening during hydration, and develop potential materials for structural use without extraordinary curing conditions. It is anticipated that this dissertation will act as a body of knowledge for future research involving Rawhide spray dryer ash. Finally, this work outlines goals of future investigations of hydrated spray dryer ash materials to evaluate long-term performance and rule out, or make provisions to prevent, sulfate attack as a defect.

1.7 Organization of the Dissertation

Chapter 2 outlines the literature concerning coal combustion by-products involving spray dryer ash specifically and fly ash where appropriate. The state of understanding regarding hydration products is provided along with research concerning the fresh and hardened properties of hydrated ash materials and ash replacements in concrete. Literature concerned with the life cycle assessment and costing of coal combustion by-products has been developed more recently and is examined here as well. Chapter 3 describes the materials and methods of testing that were used. Chapter 4 provides the results of compressive and flexural testing of the various mortars that were investigated. Chapter 5 presents a summary of the work with discussion of the results, investigates potential applications and barriers to implementation, and provides suggestions for future work. Finally, a glossary is provided with definitions of key terms and acronyms used throughout this work.

2. Literature Review

The background concerned with beneficial use of coal combustion by-products (CCBs) is vast, but it is more developed for fly ash and other CCBs than for spray dry absorber material. It reaches into the academic, industrial, environmental, and governmental sectors. Many parties have reasons to find effective ways of utilizing coal ash as a feedstock. Utilities produce much of it and do not want to store it, its production and disposal is regulated by the government, and the opportunity to close materials loops and improve process efficiency by using these materials is recognized by researchers, environmentalists, and industry partners. Literature concerning coal ash is generated by the government, utilities, transportation departments, research institutes, universities, and various industry organizations through books, peer-reviewed journals, conference proceedings, marketing documents, specifications, trade magazines and implementation guidelines. Associated biases and perspectives are present. Government data collection provides an excellent background for discussing the overall place of coal ash in the nation's energy portfolio, industry groups and utilities provide data concerning production rates, quality, and economic considerations, and universities and other research institutes provide detailed analyses of specific ashes, applications, effectiveness, and chemical, mineralogical, and engineering properties.

The introduction provided background in coal ash production and environmental considerations while the literature review section will examine the academic and industry research concerned with the beneficial use of spray dryer ash. The mechanical properties of fresh and hardened spray dryer ashes have been investigated for various potential applications. These materials can be categorized based on the percentage of ash making up the cementitious materials in a mix: 100-percent coal ash materials, structural fills, grouts and controlled low-strength materials (CLSM) use large volumes of ash in their production, while coal ash as a cement replacement in concrete and high-volume fly ash (HVFA) concrete use intermediate amounts. The work already published in these areas will be examined and used to define the expected results in this research when possible, especially for those properties that were explicitly investigated here such as compressive strength and stiffness and flexural strength. Studies of spray dryer ash will be examined specifically and followed by literature concerning Class C or high-lime fly ash as this is the most similar material to have had expanded study.

Very few studies discovered thus far have approached coal ash utilization from the perspective of using it as the sole cementitious material in a structural application. A very small number have examined traditional hydration reactions at atmospheric temperatures and pressures. Others have employed fly ash as a feedstock for alkali-activated or geopolymer materials. Still others have examined elevated temperatures, pressures, or both on the improved properties of the final hardened product. Considering that concrete, broadly used in structures and paving, makes up the greatest percentage of Portland cement use and that the offsetting of this cement provides the greatest environmental and economic advantage, the goal of this research was to find a hardened spray dryer ash product cured under atmospheric temperatures and pressures that could compete with concrete.

A controlled low-strength material is defined by ACI Committee 229 as a cementitious material having compressive strength of less than 8.3 MPa (1.20 ksi) at 28 days. CLSM researchers have sought a fly ash application, usually in geotechnical or transportation fields, that uses fly ash with little additional material. The goal in CLSM research is to obtain a highly workable product with a low but predictable strength. Some CLSM work has shown the high-strength potential for fly ash as well as other properties of interest like setting time, strength gain with time, hydration products, and so on. Review of CLSM research contributes background from the perspective that fly ash has inherent properties that can be enhanced with small additions of activating materials like lime or Portland cement. Also, the hydration chemistry of fly ash and SDA material is more accurately described in these works. Although the literature concerning SDA material is less developed, SDA material has been used successfully as a CLSM.

Investigators with intentions of replacing more than 50 percent of the Portland cement in a mix generally refer to their product as a high-volume fly ash concrete, or HVFA concrete. HVFA and cement replacement researchers focus on the offsetting of cement in a concrete mix with a goal of equivalent or improved properties in the resulting hardened product. This is approached from the perspective that concrete as a material is well-understood and its properties ought to be matched or improved by any product involving fly ash. SDA materials have not been integrated significantly into these works, although some use in these applications is reported (ACAA) and greater potential is noted by the Electric Power Research Institute (EPRI, 2007).

Excellent work with Class C fly ashes has been conducted by the Center for By-Products Research at the University of Wisconsin - Milwaukee often in conjunction with Wisconsin Energies, a very progressive utility that uses 100 percent of its CCBs. The Coal Ash Research Center (CARC), part of the Energy & Environmental Research Center (EERC) at the University of North Dakota is also an excellent resource for coal ash related literature and SDA material specifically. Proceedings of the Canada Centre for Mineral and Energy Technology (CANMET) and World of Coal Ash (WOCA) conferences provide the most up-to-date research on coal ash. The Electric Power Research Institute (EPRI), the American Coal Ash Association (ACAA), and the Environmental Protection Agency's Coal Combustion Products Partnership (C2P2) program also support or conduct active research on CCB beneficial use. The two authors with the largest contributions to fly ash use in concrete, particularly in high volumes, are V.M. Malhotra and P.K. Mehta. The most targeted literature concerning beneficial use of SDA material has been produced by Heebink et al. (2007), EPRI (2007), and Berland et al. (2003).

The literature review presented below will focus first on the history of coal ash research and classification. The hydration chemistry and products of Portland cement, fly ash, and spray dryer ash will be described. The state of knowledge of fresh and hardened material properties will be outlined along with the impact of specific studies on the work detailed here. Finally, literature concerned with the life cycle assessment of Portland cement concrete and the potential improvements in energy and emissions based on fly ash utilization will be presented.

2.1 History of Coal Ash Research and Classification

The effect of fly ash as an additive to Portland cement concrete has been studied for a considerably long time with significant change in industry practices occurring slowly and only in very specific locations where research capability and industry need were substantial. Because the bituminous coals of Ohio, West Virgina, and Pennsylvania were the earliest to be exploited and resulted in low-lime fly ash, Class F fly ash and its purely pozzolanic behavior has been given the most attention in the literature. Davis et al first addressed the topic in 1937. They even examined 50 percent cement replacement by fly ash, noting that 34.5-MPa concrete at 90 days was achievable at such a replacement rate. The first ASTM specification for low-lime fly ash (specifically what would become Class F fly ash) as a fine aggregate in concrete was adopted in 1953. A 1960 specification allowed for its use as a pozzolan in concrete. High-lime Class C fly ash was added as a classification in 1977 (Manz, 1999). High-lime fly ash and its cementitious properties have seen increased research since the early 1980s (Naik and Chun, 2003). Power plants built after 1978 employed flue gas desulferization systems to comply with Clean Air Act regulations that limited emissions of SO_2 (EPRI, 2007). The research of SDA material resulting from spray dry absorbers is thus relatively undeveloped compared to fly ash and has seen more attention since the late 1980s.

Given the wide range of properties and compositions exhibited by fly ash and associated materials, the classification of fly ash has seen much discussion in the literature. Vassilev and Vassileva (2007) provide an excellent review of suggested fly ash characterization schemes along with their own. ASTM C 618 - Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete is used often in U.S. and international studies and defines the chemical and physical characteristics of high-lime (Class C) and low-lime (Class F) fly ash for use in concrete. This specification, with its strict limit on SO_3 content, rules out the use of most spray dryer ashes in concrete due to fears of increased sulfate attack and reinforcing corrosion associated with increased chloride levels. It makes no detailed mention of coal sources, varying LOI levels (beyond a simple maximum allowable amount), or mineralogical composition and is thus criticized by many who research coal ash.

2.2 Hydration Chemistry

The hydration chemistry of traditional Portland cement, Portland cement with pozzolans, and spray dryer ash will be described here along with the mineralogical hydration products that result. While the hydration of Portland cement is well-understood, it is difficult to find literature specific to SDA material hydration because of the many terms for similar ashes and the multitude of similar products produced by different processes. For instance, a high-calcium high-sulfate fly ash could be a pure fly ash from a high-sulfur coal or a spray dryer ash from a low-sulfur coal. The mineralogy and hydration characteristics might also be different. The hydration of these products is provided primarily in the chemistry literature, while the application of the materials is discussed in industry and engineering literature with little crossover. The hydration chemistry of Portland cement will be described first to provide background for the discussion of SDA material hydration to follow.

Portland cement contains various compounds such as calcium silicate ($3CaO{\cdot}SiO_2$), calcium aluminate ($3CaO{\cdot}Al_2O_3$), and calcium aluminoferrite ($4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$) produced as described in the introduction. These compounds are absent hydrogen and dissolve readily in water. Once in solution, precipitation products begin to form including calcium silicate hydrates, calcium aluminate hydrates, calcium hydroxide, and ettringite (a calcium aluminate sulfate hydrate). This process is fairly well understood and is described in detail by Mehta and Monteiro (2006). Calcium silicate hydrates (CSH) make up the majority of the reaction products and contribute to the bulk of the strength of the final hardened product. Ettringite and calcium aluminate hydrates (CAH) form early as a result of the deliberate addition of gypsum to the cement and contribute more to setting and stiffening of the concrete mix than to strength. Their development is encouraged by design so that flash setting of the mixture does not occur. During the hydration of the calcium silicates and calcium aluminates, calcium hydroxide or hydrated lime ($Ca(OH)_2$) is liberated. This hydrated lime has relatively little strength and increases the porosity of the resulting concrete. When low-lime fly ash is added to Portland cement concrete, the excess hydrated lime reacts with the silicate and aluminate in the fly ash to produce additional CSH and CAH via pozzolanic reactions, thus reducing the permeability of the concrete and improving its durability and strength. EPRI (1997) describes the initial lime reaction and subsequent pozzolanic reactions succinctly via the following chemical equations:

$$CaO + H_2O \rightarrow Ca(OH)_2$$
$$xCa(OH)_2 + ySiO_2 + zH_2O \rightarrow xCaO \cdot ySiO_2 \cdot zH_2O$$
$$xCa(OH)_2 + yAl_2O_3 + zH_2O \rightarrow xCaO \cdot yAl_2O_3 \cdot zH_2O$$
$$xCa(OH)_2 + ySiO_2 + zAl_2O_3 + wH_2O \rightarrow xCaO \cdot yAl_2O_2 \cdot zSiO_3 \cdot wH_2O$$

This process occurs with high-lime fly ash as well, although the presence of lime in the fly ash gives it self-cementing properties of its own and reduces the silicate, aluminate, and ferrite available for pozzolanic reactions.

As noted above, needle-shaped ettringite is one of the first hydration products of Portland cement and contributes to stiffening of the fresh cement paste. Ettringite is also the primary early hydration product of SDA material, although the hydration chemistry is not as clearly understood as that for Portland cement concrete. SDA material is composed primarily of calcium sulfites and sulfates, lime, and aluminate, which are the building blocks of ettringite (also known as the AFt phase or trisulfate). Monosulfate (or the AFm phase) is a stable higher-density hydration product that can be produced and often develops later in Portland cement concrete (Motzet and Pollmann, 1999; Lecuyer et al., 1996; Solem-Tishmack et al. 1995). Both contain significant amounts of water, which can be seen in the chemical formula below.

EPRI (1997) describes the reactions that form ettringite:

$$3CaO + Al_2O_3 + 3CaSO_4 + 32H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \text{ (ettringite)}$$

Some suggest that this product is relatively stable, while others note the potential for ettringite to dissolve and reconstitute under certain highly alkaline or hot and wet environments causing expansion. If additional sulfate ions are made available to monosulfate after the concrete has hardened it can revert to the lighter density ettringite form and cause expansion. Additionally, the calcium aluminate hydrates (CAH) can combine with sulfate in solution to produce ettringite. When the sulfate solution permeates the concrete from the outside, the process is referred to as conventional sulfate attack (Sharp, 2006).

Similar reactions are known to occur if sulfate ions are present in the concrete matrix itself. When this is the case, the attack is called delayed ettringite formation (DEF) (Sharp, 2006). DEF can occur when ettringite formed during hydration is decomposed and reformed or when new ettringite is formed in the presence of lime, sulfates, water, and relatively high temperatures (>65 – 70 ^{o}C) well after the concrete is set. DEF usually occurs in gaps and cracks created when the expansion occurs and effectively detaches the cement paste from the aggregate resulting in further weakening of the concrete structure. There is worry among many researchers that internal DEF will result if SDA material is used in a cementitious matrix due to the elevated levels of sulfate it introduces. It is unclear whether cement paste expansion occurs as a result of, or along with, ettringite formation, but the two often occur simultaneously and result in weakening because ettringite is weaker than monosulfate or CAH and because the cracks produced during expansion break the bond of the cement matrix around the aggregates (Tishmack et al., 1999; Mehta and Monteiro, 2006). The underlying mechanisms are still heavily debated, and thus any products involving ettringite are utilized with trepidation by industry (Sharp, 2006).

Some users of spray dryer ash have warned that their product not be subject to moisture to protect against DEF, although this may simply be a precaution (EPRI, 2007). SDA material has also been shown to hydrate and form ettringite without swelling (EPRI, 2007). However, there are no comprehensive studies on the hydration products of SDA material and their long term performance under different environmental conditions. Further, the environmental conditions affecting Portland cement concrete over long periods are still actively researched with many underdeveloped theories in place. A better understanding of favorable and detrimental conditions under which ettringite can operate will allow for more effective and longer-term use of hydrated SDA material.

Literature reviewed by EPRI (2007) indicates in numerous reports that thaumasite may be produced when SDA material is hydrated. Thaumasite is a product of sulfate and carbonate and, while once considered rare, is responsible for another form of sulfate attack (called thaumasite sulfate attack or TSA) that is currently poorly understood. Thaumasite is a chalky mineral formed via the following reactions that include the prominent compounds in spray dryer ash plus CO_2 and a significant amount of water (EPRI, 1997):

$$2CaO + 2SiO_2 + 2CaSO_4 + 2CaCO_3 + 30H_2O \rightarrow 2CaO \cdot 2SiO_2 \cdot 2CaSO_4 \cdot 2CaCO_3 \cdot 30\ H_2O \text{ (thaumasite)}$$

Thus, thaumasite occurs when sufficient sulfate, carbon, moisture and favorable pH are available in a cementitious system. When other hydration products are converted to thaumasite, a very weak material with microstructural and chemical similarities to ettringite is the result (Sharp, 2006). A number of attempts to produce hardened products with SDA material (albeit European SDA material without much fly ash) resulted in thaumasite formation under certain conditions leading the researchers to abandon the work (EPRI, 2007).

Another common compound in most spray dryer ashes is calcium sulfate hemihydrate, which can be used to retard the set in concrete mixtures. However, it is absent from the X-ray diffraction analysis performed on the Rawhide Power Station ash used in this study (discussed in detail in the Experimentation chapter), thus it is not likely that slow setting will be a concern in the materials developed here (EPRI, 2007; BASF, 2008).

The potential reactions discussed above may simply mean that hydrated SDA material should be limited in its application to dry environments rather than be left unused entirely. This background indicates that the material considered in this study should be further investigated with respect to these potentially damaging long term reactions.

2.3 Material Properties

Little information is available concerning the fresh material properties of SDA material or concrete with added SDA material. Both Class C and Class F fly ash addition to concrete has been proven in many cases not to be detrimental to fresh and hardened concrete properties and is often integral to the impressive properties exhibited by high-performance concretes. Class C and Class F fly ashes improve properties differently when added to a traditional Portland cement concrete, and are effective only in properly proportioned mixes. Class F fly ash addition to concrete is the most widely researched, but Class C fly ash is most similar to the spray dryer ash investigated here. Thus, the following subsections will focus on Class C or high-lime fly ash. The particular properties that are of common concern in concrete mixes are those of fresh concrete and those of hardened concrete. Fresh concrete properties include workability, cohesiveness, bleeding, segregation, air-entrainment, time of setting, and temperature rise. Hardened concrete properties include strength, stiffness, bonding and durability.

2.3.1 Fresh Material Properties

The inclusion of fly ash in concrete generally improves workability and reduces water requirements, bleeding and segregation (ACI 232.2, 2003). Improved workability and decreased water demand in fly ash concrete is understood to be a product of the ball-bearing effect of the spherical fly ash particles as well as dispersion of cement particles in the presence of fly ash similar to the effect of conventional water-reducing admixtures (Naik and Chun, 2003; Malhotra and Mehta, 1996). Cement particles are jagged and prone to flocculating, which creates voids and bleed channels that trap mix water and necessitate more water for good workability (Malhotra and Mehtta, 1996). Fly ash particles with their finer and more uniform particle size distribution fill these voids and break up the flocs. This serves to (1) reduce water that is otherwise required to fill void spaces and promote workability, (2) encourage workability via ball-bearing effect, and (3) densify the paste and improve the aggregate-paste transition zone, preventing bleed channels and segregation (Naik and Chun, 2003). These improved properties are recognized for fly ash-only mixes as well. Cross et al. (2005) report excellent workability and finishing of their 100-percent Class C fly ash material. An average slump of 102 to 152 mm (4 to 6 in) was achieved with a very low water-to-Class-C-fly-ash ratio of 0.23. Similar behavior is expected of the SDA material considered here given that it shares many chemical and physical characteristics with Class C fly ash.

Naik and Chun (2003) indicated that fly ash concrete required additional air entraining agent to ensure good freeze-thaw performance. The primary reasons cited were unburned coal (or LOI) in fly ash that adversely affected air entraining admixtures and increased fly ash fineness, which encouraged greater density, although the literature available is very limited. Naik and Chun also reported that literature concerned with setting times of high-volume Class C fly ash concrete showed mixed results with respect to set time. However, very high cement replacements with fly ash had a tendency to flash set. Cross et al. (2005) also noted this tendency with their 100-percent hydrated Class C fly ash concrete and used Borax to retard the set. Malhotra and Mehta (1996) noted the tendency of very fine mineral admixtures in large quantities to cause stickiness due to close particle packing.

Reduced heat of hydration was one of the first properties of fly ash in concrete to be exploited (ACI 232.2, 2003). By slowing the early rate of reaction in a large monolithic concrete pour and extending the later pozzolanic reactions, extreme differential cooling and resulting cracking can be limited. Mehta reported that high-lime fly ashes may cause an increase in the heat of hydration and encourage rapid setting in concrete mixtures due to their increased reactivity (1989). EPRI (1997) reported that hydrated SDA material did not exhibit high heat of hydration in their testing, possibly due to the different hydration products that were produced compared to high-lime fly ashes.

2.3.2 Hardened Material Properties

Compressive, splitting tensile, flexural, and fatigue strength, modulus of elasticity, and creep and shrinkage behavior are the hardened properties that are most useful to engineers. Durability considerations such as permeability, abrasion resistance, carbonation and corrosion of steel reinforcement, freeze-thaw performance, salt-scaling resistance, alkali-silica reaction, and sulfate attack (conventional, delayed ettringite formation, and thaumasite form) are also major concerns. The time rate of change of hardened properties is also often a significant concern as the usual goal of structural concrete is to cure as quickly and completely as possible under a variety of conditions. The hardened properties of hydrated spray dryer ash can vary depending on the chemical, mineralogical, and physical nature of the ash. This variation is much better covered in literature concerning fly ash and will be explored here, although the unique chemical and mineralogical properties of spray dryer ash can produce very different results. General statements regarding addition of cement, lime, or other activators can be made, but long-term behavior, especially for hydrated spray dryer ashes is not widely available. There is slightly more information available concerning the hardened properties of SDA material, compared to fresh properties, given the attempts of departments of transportation to use the material in structural fills, grouts, and as a cement replacement in concrete. EPRI (1997) provided the most extensive results, but variations in water-to-ash ratios and testing of pure pastes makes direct comparisons somewhat difficult.

In a study of spray dry absorber material for grout applications, SDA material was mixed with cement in ratios of 2-to-1, 1-to-1, and 1-to-3 with relatively high water-to-cementitious ratios between 0.55 and 0.88 (EPRI, 1997). The correlation of compressive strength to the water-to-cementitious ratio was much stronger than that of the ash-to-cement ratio. Sufficient parametric testing was not performed to fully describe these correlations. The most impressive results were obtained from a 1-to-1 ash-to-cement ratio and water-to-cementitious ratio of 0.51. The 7-day and 28-day strengths were 13.8 and 26.1 MPa, respectively. These are reasonable strengths for general use concrete, but other properties of this material were not provided in the EPRI report. It will be shown here that similar strengths can be reached with much less cement and a lower water-to-cementitious material ratio of 0.4.

In a study of pure hydrated SDA material for structural fill applications, the moisture content was intentionally maintained around the optimum moisture content, which generally corresponds to a water-to-ash ratio between 0.2 and 0.4. The hydrated spray dryer ashes were moist cured and showed 28-day strengths between 0.14 and 5.45 MPa (EPRI, 1997). These results showed significant variability and the details of the ash composition were not provided. The hydrated ash mortars tested for this dissertation had greater strength even on the high end of the water-to-ash ratios in the study described above.

Some research is available to evaluate SDA material as a cement replacement in concrete (EPRI, 2007). In studies with high volume fly ash addition to concrete, the higher CaO content of Class C and other high-lime fly ashes has been shown to improve the strength of the concrete and allow for greater cement replacement levels when compared to Class

F and low-lime fly ashes (EPRI, 1997). Given the high levels of lime in SDA material, similar results should be expected when it is added to concrete.

In a study of SDA material as a cement replacement, the ratio of SDA material-to-cementitious material ratio was 0.31 and the water-to-cementitious ratio was 0.45 (EPRI, 1997). The SDA materials met ASTM C 618 specifications except for the SO_3 contents, which were 10.25 and 12.25 percent in two samples. While the use of SDA material in this study (EPRI, 1997) was relatively small, the results suggest that it can be used effectively as a cement replacement in Portland cement concrete. The fresh concrete had good slump values (10.2 cm). While the initial setting of the SDA material samples was slower than the control, the samples incorporating SDA material had compressive strengths greater than the control concrete at all ages between three and 90 days. The moduli of rupture were lower than for the control concrete (4.1 and 4.3 MPa versus 5.3 MPa for the control), which is the only area where the spray dryer ash-added concrete properties fell short of the control. Results of freeze-thaw testing showed excellent durability factors (99.3 and 94.2 compared to 92.5 for the control) and reasonable length changes (0.04% versus -0.02% for the control). The individual hydration products were not discussed and sulfate attack was not examined.

Another test performed to investigate SDA material addition to a 27-MPa (4-ksi) design strength concrete showed improved compressive strength results at all ages from three to 94 days with low cement replacement levels of five and 10 percent (EPRI, 1997).

Little (2008) investigated the same Rawhide Power Station SDA material used here as a cement replacement. He showed that cement replacements up to 45 percent produced compressive strengths that exceeded those of a control concrete mixture. Specimens with 55 percent replacement were slightly weaker at 28 days and all mixes with SDA material replacing cement had lower strength at one day, which is consistent with the slow strength gain reported of fly ash concrete (ACI 232.2, 2003). Even with 55 percent cement replacement with SDA material, a 28-day strength of 27 MPa (4.0 ksi) was achieved.

SDA material with very high SO_3 content (between 13 and 26 percent) and high CaO content (around 30 percent) was hydrated at a 0.4 water-to-ash ratio for a study of road base materials in Minnesota (Behrens et al., 1997). Compressive strengths according to ASTM C 109 were reported to be 0.41 MPa, 2.14 MPa, 10.36 MPa, and 15.04 MPa at 1, 3, 7, and 14 days respectively. These are impressive results for a pure hydrated ash paste. The water-to-ash ratio was the same as that used for the work presented in this dissertation, so the results published by Behrens et al. (1997) can provide a good comparison for the results generated here. The sulfate content was considerably higher in the Behrens et al. (1997) study than for the ash investigated here and it is uncertain what impact this had, although other research suggests that the higher sulfate levels will encourage ettringite and thaumasite formation. The impact of these hydration products has not been studied comprehensively in a joint chemical/engineering investigation and was not explored by Behrens et al. (1997).

Solem-Tishmack et al. (1995) tested hydrated SDA material, high-lime fly ash and fluidized bed combustion (FBC) fly ash as hazardous waste binders for selenium and borate. Ettringite was desired to act as the primary binder for the waste product. The control specimens for this study are of the greatest interest here. The water-to-ash ratio used for the SDA paste was 0.45. Compression testing was conducted on ASTM C 109 cube specimens of hydrated pastes yielding strengths of 1.6 MPa at 7 days, 2.9 MPa at 28 days, and 4.6 MPa at 91 days for the SDA material. The fly ash pastes were significantly stronger (up to 30 MPa at 28 days). Ettringite formation was measured at around 20 percent for each of the SDA material specimens, which was more than double that of the fly ash specimens and less than that of the FBC ash. Expansion was negative, progressing from -0.09% at seven days to -0.12% at 91 days, while the fly ash specimens showed little to no expansion and the FBC ash showed nearly three percent expansion at 91 days. Ettringite formation did not necessarily correlate with weaker compressive strength, so the results of this study, while interesting, do not provide sufficient background in themselves to draw conclusions about the mechanisms for strength gain in SDA materials. Given that ettringite made up only 20 percent of the hydration products, CSH and CAH are likely to have made up the rest. The compressive strengths were significantly lower than those found by Behrens et al. (1997), which shows the relative variability of the hydrated ashes. The fact that the water-to-ash ratio was slightly higher in this study may also be cause for the reduced compressive strengths that were measured.

Butalia et al (2001) produced pure hydrated SDA flowable fill with high water content and very low unconfined compressive strength to ensure easy excavation. Based on the poor early penetration resistance, Butalia et al. determined that the pure hydrated SDA material did not have sufficient quick set characteristics to support anticipated construction loads. The compressive strengths measured in this study were extremely low (less than 0.35 MPa) and the water-to-ash ratios were significantly higher (0.65 to 0.77) than that used here (0.4). Thus, the Butalia et al results are not reasonable for comparison to the results generated here, but Butalia et al (2001) show the potential for CLSM applications of SDA material if quick set properties can be developed or if higher final-strength material will suffice.

Cross et al. (2005, 2008) produced a 100-percent Class C fly ash concrete with excellent compressive strength (20 MPa at 2 days, 32 MPa at 28 days, and 55 MPa at one year). Their fly ash had only 2.02 percent SO_3, but 28.89 percent CaO, and low LOI. It is unclear what gave this ash its truly exceptional hydrated properties. Mineralogical analysis was not provided. The authors noted that ACI equations relating flexural strength and modulus of elasticity to the compressive strength were reasonably accurate.

Naik and Chun (2003) summarized the results of previous studies to develop HVFA concrete with high-lime fly ash (Table 2.1). In general, results showed that 50-percent cement replacement by high-lime fly ash was not detrimental to the compressive strength, and optimal replacement levels were 35 to 40 percent. Some studies showed improved strengths with cement replacement levels up to 75 percent. In some cases, very low water-to-cementitious ratios were achieved with the use of superplasticizers and water reducing admixtures, contributing to the enhanced strength with equivalent workability. Modulus of elasticity trends for HVFA concretes tended to follow compressive strength as would be expected. However, when experimental moduli were compared to the ACI 318 equation relating modulus of elasticity to compressive strength, the results were variable with some moduli high and some low depending on the study.

Creep and shrinkage were reported to decrease in the majority of studies investigating Class C fly ash inclusion in concrete. This was attributed to lower water-cementitious ratios required of these mixes and the resulting denser microstructure. Good resistance to water, air, and chloride ion permeability was reported in numerous studies for HVFA concretes employing Class C fly ash. Abrasion resistance was reported to be reduced in most cases of high volume fly ash inclusion. It is worth noting this deviation from many of the otherwise improved or equivalent properties shown by HVFA concretes. Freeze-thaw performance was reported to be as good in HVFA concrete as in traditional Portland cement concrete in most cases (Naik and Chun, 2003).

Salt-scaling generally occurs on the surface of concrete when standing water, often with a solute, freezes and thaws causing superficial damage. This behavior is dependent on the permeability of concrete and can become more pronounced with the finer pore structure of HVFA concretes. Alkali-silica reaction occurs when aggregates containing amorphous silica react in a highly alkaline cement paste causing expansive products. Class F fly ash is known to reduce this behavior when added at levels above 25 percent. Class C fly ash can promote the reaction if it contributes water-soluble alkali sulfates to the cement paste (Mehta and Monteiro, 2006; Naik and Chun, 2003). This may be a concern with SDA material, but it has not been actively researched.

Table 2.1. Effect of high-lime fly ash as a cement replacement in Portland cement concrete according to literature reviewed by Naik and Chun (2003).

Property	High-lime HVFA compared to Traditional Portland Cement Concrete
Compressive Strength	Mixed with some improvements reported
Tensile Strength	Reduced
Modulus of Elasticity	Mixed
Creep and Shrinkage	Improved (i.e. reduced creep and shrinkage effects)
Permeability	Mixed, but mostly improved
Abrasion Resistance	Reduced
Carbonation and Rebar Corrosion	Improved, but based on relatively few studies
Freeze-Thaw Performance	Equivalent to improved with adequate air entrained
Salt-Scaling Resistance	Mixed, numerous cases of poor performance
Alkali-Silica Reaction	Mixed, but based on relatively few studies
Sulfate Resistance	Mixed, but improved with ettringite production as a stable product of hydration and reduced CAH and monosulfate
Fatigue Strength	Insufficient data

The materials investigated for this dissertation had a fibrous component as well as a cementitious one. Thus, the literature of fiber-reinforced brittle matrix composites was examined. Polymer fibers have been used since the 1970's in concrete and other cementitious products to control cracking during setting. They are recognized to improve toughness, but they have variable results with respect to strength and stiffness (Balaguru and Shah, 1992; Johnston, 2001). Few specific expectations can be made based on available literature given the poor characterization of the fibers that were used and the unknown nature of the matrix materials.

2.4 Life Cycle Considerations

The consideration of life cycle is important as alternatives to structural concrete and other Portland cement based products are investigated. In general, any alternative to Portland cement will be an improvement, given its significant energy requirements and greenhouse gas emissions. However, considering the details of a product life cycle is critical to determining a best practice with respect to environmental impact based on emissions and energy use. Consideration of a product's life cycle costs can capture externalized environmental costs that are often not accounted for or are at least not obvious to a buyer or user. While the capitalist system is excellent at determining a fair market price for goods and services, prices usually do not account for environmental degradation, the costs of which are borne often by governments and the poor. Development of life cycle assessment as well as cost tools can begin to capture all of the various costs and impacts of a product such that its price will accurately reflect the impact of the product in economic, social, and environmental terms from cradle to grave. Life cycle assessment and costing will be considered here in principle, with limited rigor. Recommendations for the best possible use, or uses, of the spray dryer ash produced at the Rawhide Power Station will be made based on this background in Chapter 5.

Life cycle assessment (LCA) is defined by the International Organization for Standardization (ISO) in ISO 14040, a widely used standard that specifies LCA principles and framework:

> "... a technique for assessing the environmental aspects and potential impacts associated with a product, by compiling an inventory of relevant inputs and

> outputs of a product system; evaluating the potential environmental impacts associated with those inputs and outputs; interpreting the results of the inventory analysis and impact assessment phases in relation to the objectives of the study. LCA evaluates the environmental aspects and potential impacts throughout a product's life (i.e. cradle to grave) from raw material acquisition through production, use and disposal. The general categories of environmental impacts needing consideration include resource use, human health, and ecological consequences."

The components of an LCA under ISO 14040 are goal and scope definition and inventory analysis (ISO 14041), life cycle impact assessment (ISO 14042), and life cycle interpretation (ISO 14043). Glick (2007) notes the potential of LCA to provide benefits to society based on the relatively small cost of an LCA being borne by a few. He also points out some of the weaknesses of LCA as an objective measure: primarily, that human values are involved in all aspects. Glick states, however, that value-free scientific data is not completely necessary if LCA provides answers to specific questions about building products and considers the direction of environmental indicators. Fundamental weaknesses cited by Glick and others include inaccurate or outdated process data, imprecise system boundaries, and the relative complexity of analyzing processes and impacts. Comparisons of individual products up to the point of delivery to market (i.e. from cradle to gate) can be easier to evaluate, while analyzing those products for use and disposal (i.e. cradle to grave) adds complexity. Cradle to gate analyses will be considered here to maintain generality and allow comparisons of products that are likely to have the same use and disposal impacts. Life cycle inventory data concerning Portland cement production is disparate and often more widely available for countries other than the United States.

Given the similarities in handling and production of fly ash and SDA material, these materials can be considered equivalent in terms of LCA. The United States Environmental Protection Agency (EPA, 2008) provides some direction on how fly ash and SDA material should be considered as raw materials in concrete products:

> "coal fly ash generally does not require grinding prior to its beneficial use in concrete and is therefore modeled as an environmentally "neutral" input to concrete production. Thus, the benefits of coal fly ash substitution directly represent the environmental benefits associated with avoiding the production of one metric ton of portland cement."

Fly ash is handled this way by all of the authors discovered in this review. While SDA material requires the input of a lime sorbent to the desulferization process, the impact of this should be borne by the electricity product and SDA material should be considered a neutral by-product like fly ash. Given this approach, the impact of Portland cement becomes the primary factor in an LCA of a concrete product derived from SDA material as the cement has production impacts while those associated with the ash are borne entirely by the primary product: electricity. A number of authors have addressed life cycle impacts of cement and concrete production (EPA, 2008; Lippiat and Ahmad, 2004; Huntzinger and Eatmon, 2009; Martin et al., 1999; Flower and Sanjayan, 2007; Reiner, 2007). Cement replacement by fly ash in a given product should be evaluated on a case-by-case basis taking into account local variations in cement production efficiency and ash handling and delivery among other details. While complete life cycle analysis of various beneficial use applications for SDA material is beyond the scope of this dissertation, the life cycle inventory data regarding Portland cement production provide a starting point for considering various replacement levels or alternative products.

The CO_2 equivalent emissions generated during Portland cement clinker production are often reported as one tCO_2e/tonne, or one-to-one by mass. The EPA (2008) stated that one metric ton of Portland cement produces 0.72 metric tons of CO_2 equivalent emissions of which 0.70 is CO_2. Flower and Sanjayan (2007) working in Australia placed this number between 0.74 and 0.81, and used 0.82 when transportation to the batching plant was included. They also used an emissions factor for fly ash 0.027 tCO_2e/tonne taken from Heidrich et al (2005) that included the capture, milling, refining and transport (100 km) processes. Reiner (2007) evaluated the embodied energy and CO_2 emissions for Portland cement manufactured in 2004 in the U.S. (5.02 GJ/tonne and 1.01 tCO_2e/tonne) and regionally in Colorado (5.02 GJ/tonne and 1.05 tCO_2e/tonne), with much higher estimates. He stated that the disparity was due to the wide boundaries set in his LCA, but he effectively confirmed the one-to-one ratio of CO_2e emitted to cement produced that is so widely reported. His embodied energy numbers were higher than other sources reported as well. Mehta and Monteiro (2006) reported 4 GJ/tonne. These numbers have wide variation and can be found in numerous sources.

Impressive improvements have been noted with respect to CO_2 emissions and energy required for Portland cement clinker production recently. Martin et al (1999) reported that the energy required for production, CO_2 emitted due to fuel consumption, and CO_2 emitted due to calcination decreased by 30, 25, and 17 percent from 1970 to 1997. However, Reiner (2007) and Huntzinger and Eatmon (2009) cite that nearly half of the greenhouse gas emissions (0.507 tCO_2e/tonne of cement) is a result of calcination during the clinkering process and cannot be reduced without impacting the quality of the clinker. Thus, further improvements in the emissions associated with concrete production must come via energy efficiency and reductions in Portland cement content in concrete. Direct replacement of cement clinker by fly ash, spray dryer ash, or other industrial by-products provides an effective means to make the necessary improvements in energy and emissions.

The software package BEES (Building for Environmental and Economic Sustainability) developed by the National Institute of Standards and Technology and the Building and Fire Research Laboratory is used often to quantify life cycle assessment variables and costs, and has provisions for concrete with fly ash replacement levels up to 35 percent (EPA, 2008; Lippiat and Ahmad, 2004). According to this software, the CO_2 emitted during manufacture of a 27-MPa reinforced concrete is 13.581 kg per cubic foot, which corresponds to an emissions factor of 0.202 tCO_2e/tonne of concrete. If 100 percent of the Portland cement is offset with a pure coal ash binder (assuming equivalent performance), the emissions are 0.0759 tCO_2e/tonne, which means that Portland cement accounts for 63 percent of the emissions in concrete. The remaining emissions are attributed to aggregates, processing, and reinforcing steel and can be further reduced if recycled aggregates or no aggregates are used, which was the case for some of the materials investigated here that included fibers.

Life cycle analyses often incorporate more impacts than simply energy and CO_2 emissions, although these are usually the greatest concerns. Reiner (2007) calculated the emissions saved by avoided landfilling of fly ash to be 0.018 tCO_2e/tonne based on transportation and equipment operation at the fill site. The monofill at the Rawhide Power Station is approximately one mile from the silo and other grading equipment is used rarely, so this benefit is likely much less for the SDA material considered here. The emissions of other toxics and water also contribute to the environmental impact of a process. The EPA (2008) examined the savings in various emissions when various so-called recovered mineral components (fly ash, ground granulated blast furnace slag (GGBFS), or silica fume) were substituted for Portland cement in concrete (Table 2.2).

Table 2.2. Life cycle impacts per metric ton of recovered mineral components substituted for finished Portland cement in concrete (EPA, 2008).

Metric	---Material---		
	Coal Fly Ash[a]	GGBFS	Silica Fume[b]
Energy Savings (megajoules)	4,695.9	4,220.9	32,915.0
Energy Savings (US $)	129.1	116.1	905.2
Water Savings (Liter)	376.3	145.2	-5,111.4
Water Savings (US $)	0.2	0.1	-3.2
Avoided CO_2 Equivalent (GHG) (grams)[c]	718,000.0	*Not calculated*[e]	
Avoided CO_2 Emissions (grams)	701,377.7	668,889.1	699,923.3
Avoided CF_4 Emissions (grams)	0.0	*Not calculated*[e]	
Avoided CH_4 Emissions (grams)	594.8		
Avoided N_2O Emissions (grams)	13.2		
Passenger cars not driven for one year[d]	0.2		
Passenger cars and light trucks not driven for one year[d]	0.1		
Avoided gasoline consumption (liters)[d]	310.0		
Avoided oil consumption (barrels)[b]	1.7		
Avoided NOx Emissions (grams)	2,130.2	2,014.8	28,442.2
Avoided PM_{10} Emissions (grams)	0.0	0.0	-0.1
Avoided SOx Emission (grams)	1,673.9	1,605.8	42,560.1
Avoided CO Emissions (grams)	654.3	621.5	2,278.2
Avoided Hg Emissions (grams)	0.0	0.0	-0.3
Avoided Pb Emissions (grams)	0.0	0.0	0.6
Avoided biochemical oxygen demand in water (grams)	3.4	-0.8	-21.0
Avoided chemical oxygen demand in water (grams)	28.7	-6.5	-201.4
Avoided copper water emissions (grams)	0.0	0.0	0.0
Avoided suspended matter in water (grams)	15.4	-3.5	-55.1
Avoided emissions to soil (grams)	0.0	0.0	0.0
Avoided end of life waste (kilograms)	0.0	0.0	0.0

Notes:
a. Impact metrics based upon representative concrete products.
b. Negative values represent an incremental increase in impacts relative to the use of portland cement.
c. Avoided CO_2 equivalent is an expression of the cumulative global warming potential of all four greenhouse gasses for which BEES data were available (CO_2, CF_4, CH_4, and N_20). It can be calculated from the global warming potentials of individual greenhouse gasses, using the global warming potential of $C0_2$ as the reference point. Avoided CO_2 equivalent was calculated using the Greenhouse Gas Equivalencies Calculator developed by the U.S. Climate Technology Cooperation (accessed at: http://www.usctcgateway.net/tool/).
d. The greenhouse gas metrics taken from BEES were converted to equivalent impacts such as passenger cars removed from the road for one year, passenger cars and light trucks removed from the road for one year, avoided gasoline consumption, and avoided oil consumption, using the Greenhouse Gas Equivalencies Calculator. It is important to note that these metrics are equivalent expressions of the avoided greenhouse gas metrics reported by BEES; they do not represent additional benefits.
e. GHG equivalency metrics were not calculated for GGBFS and silica fume, due primarily to the fact that use of these materials is unlikely to change significantly across scenarios.

The literature reviewed indicates that the properties of spray dryer ash, like those of fly ash and other cementitious materials, are highly dependent on the chemical, mineralogical and physical characteristics of the ash and additives and the water-to-cementitious material ratio. The 28-day compressive strength of hydrated spray dryer ash could fall anywhere between 0.14 and 15.04 MPa based on the literature reviewed. This is a wide range and makes additional work regarding hydrated spray dryer ash very valuable. While many studies investigate nominal cement replacements in a concrete mix, none of the studies discovered in this review considered small additions of Portland cement to spray dryer ash with the intent of achieving compressive strength sufficient for structural use. Thus, the results of this dissertation contribute substantially to the understanding of spray dryer ash and its potential in structural applications.

3. Experimentation

3.1 Materials

3.1.1 Spray Dryer Ash

The ash used in this study was obtained from the Rawhide Power Station (RPS) in northern Colorado, which is under the management of the Platte River Power Authority (PRPA). Low-sulfur sub-bituminous coal from the Powder River Basin is burned at RPS to run a 274-MW coal-fired steam turbine generating electricity for northern Colorado communities (Little, 2008). RPS was put into service in 1984 and adopted spray dry absorber (SDA) technology to manage SO_x emissions. The plant's flue gas desulfurization (FGD) process, or SDA system, employs high-calcium fly ash resulting from the coal combustion and supplemental lime as sorbents for SO_2 and SO_3 in the flue gas. This results in a so-called spray dryer ash with increased levels of SO_3 and CaO (David Goss, personal communication). Because RPS requires low-sulfur coal (design sulfur content is 0.30 wt% (EPRI, 2007)), even with the SDA process, the resulting SO_3 content in chemical analyses of the ash is around 5 percent, very close to the maximum specified in ASTM C 618. However, the mineralogical content of the ash is very different than a Class C fly ash produced at a plant without flue gas desulfurization as will be discussed further below.

The properties of coal combustion ashes have historically been reported in terms of their chemical composition. While this is important to place an ash in context with previous studies, the physical and mineralogical characterizations of an ash have a more significant impact on its classification and potential use. A complete description of the chemical, mineralogical and physical properties of the ash used in this study will be given below.

3.1.1.1 Chemical Properties

The chemical composition of the fly ash used in this study is provided in Table 3.1 for three separate samples taken between 2007 and 2008. The combined percentage of SiO_2, Al_2O_3, and Fe_2O_3 is 59.6 percent for Sample 1 and 60.63 percent for Sample 3, which exceed the 50 percent minimum for Class C fly ash (ASTM C618). Sample 2 falls just below this limit at 49.9 percent. The very high lime content (23.45% and 26.48% CaO) in this fly ash gives it self-cementing properties and increases the likelihood of reactive components at early ages (ACI 232.2, 2003). However, the lime in the chemical characterization is likely bound up with sulfur as a result of the SDA process; this is described further in the mineralogical analysis. The low level of free lime in the ash was confirmed in an analysis by Wyoming Analytical Laboratories (2007) that showed the free lime content in the ash to be 0.10 wt%.

Table 3.1. Bulk chemical composition of Rawhide Power Station fly ash (SGS, 2007; Wyoming Analytical Laboratories, 2007; Little, 2008).

Compound	Sample 1 Content[A] (%)	Sample 2 Content[B] (%)	Sample 3 Content[C] (%)	ASTM C618 limit for Class C Fly Ash (2005)	ASTM C 618 limit for Class F Fly Ash (2005)
Silicon Dioxide, SiO_2	39.76	29.84		Sum between 50 % and 70 %	Sum greater than 70 %
Aluminum Oxide, Al_2O_3	14.31	14.24			
Iron Oxide, Fe_2O_3	5.56	5.82			
$SiO_2 + Al_2O_3 + Fe_2O_3$	59.63	49.90	60.63		
Calcium Oxide, CaO	23.45	26.48			
Sulfur Trioxide, SO_3	6.19	10.01	3.70	5 % maximum	5 % maximum
Magnesium Oxide, MgO	4.06	4.93			
Sodium Oxide, Na_2O	1.42	1.66			
Titanium Dioxide, TiO_2	1.15	0.98			
Phosphorous Pentoxide, P_2O_5	0.98	1.59			
Barium Oxide, BaO	0.61	0.68			
Potassium Oxide, K_2O	0.53	0.48			
Strontium Oxide, SrO	0.33	0.42			
Manganese Dioxide, MnO_2	<0.01	0.02			
Moisture	1.86	1.04	1.33	3 % maximum	3 % maximum
Loss on Ignition	1.65	2.85	1.64	6 % maximum	6 % maximum

A – Sampled 4/3/2007 and tested by SGS North America, Inc., Denver, CO.
B – Sampled 7/26/2007 and tested by Wyoming Analytical Laboratories, Inc., Golden, CO.
C – Reported in Little, 2008

The ash has a high sulfate content as a result of the flue gas desulfurization process. The content has been measured between 3.70 and 10.01 percent and is in excess of the 5-percent limit for fly ash use in concrete specified by ASTM C 618 in two of the three cases reported in Table 3.1. These values are relatively low for an SDA material because low-sulfur coal is burned at the Rawhide Station. The intent of the ASTM C 618 SO_3 limit is to prevent potential sulfate attack in cement pastes of Portland/fly ash concretes (Malhotra and Mehta, 2008). While this has discouraged PRPA from marketing its ash extensively, it should not be considered cause for stockpiling this fly ash rather than finding a beneficial use (Hoffman, nd.). It has been reported that fly ashes with sulfate contents in excess of five percent have performed satisfactorily in concrete mixtures (Malhotra and Mehta, 2008). In fact, PRPA is already supplying SDA ash to a local manufacturer of architectural brick who replaces 35 percent of the cement in his mix with PRPA's ash (PRPA, 2007; Little, 2008).

The loss on ignition (LOI), a measure of unburned carbon, at 1.65 or 2.85 percent is low for fly ash in general, but relatively high for an ash that if not for its high sulfur content would be classified as Class C (ASTM, 2008). Higher LOI has detrimental effects on hydration, water requirements and strength when ash is used in traditional concrete mixes (ACI 232.2, 2003). The LOI levels of this ash are far below the ASTM C 618 limit of six percent, thus the detrimental effects of LOI are expected to be negligible.

3.1.1.2 Mineralogical Properties

While the chemical composition and ASTM C 618 classification are often all that is reported to describe a particular fly ash, the physical characteristics, mineralogical composition, and proportion of glassy or crystalline phases present are more important in understanding the properties of the fly ash in concrete (Malhotra and Mehta, 2008). Crystalline phases normally present are quartz, periclase, lime, calcium aluminate, calcium sulfate, and alkali sulfate, while glassy phases make up the majority. An X-ray diffraction (XRD) analysis of the SDA material from the Rawhide Power Station was performed for PRPA by BASF in 2008. According to the analyst at BASF, the analysis showed a mineralogical structure typical of SDA materials, namely calcium sulfites and sulfates: hannebachite ($2CaSO_3 \cdot H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), and anhydrite ($CaSO_4$). These minerals were present in addition to the common structure of ashes from Powder River Basin coals. Calcium sulfate hemihydrate ($2CaSO_4 \cdot H_2O$) and calcium hydroxide or hydrated lime ($Ca(OH)_2$) were not visible in the XRD analysis, further indicating that free lime has been hydrated and bound up with sulfates. Lime from the SDA process, while often encapsulated within a glassy phase calcium-sulfur mineral, is still available for potential reaction (BASF, 2008). These results indicate that the semidry scrubbing process is functioning effectively, and the results of this dissertation indicate that the ash functions well as a cementitious material despite the relatively high sulfur levels.

3.1.1.3 Physical Properties

The specific gravity of the ash used in this study was measured as 2.71 g/cc (SGS, 2007), which is consistent with the average density for sub-bituminous coal fly ash (ACI 232.2, 2003) and is on the high end of the range reported in the literature for SDA materials (EPRI, 2007). While hollow spheres (cenospheres) can form in fly ash, high-lime fly ash tends to have smaller particles and fewer cenospheres (ACI 232.2, 2003).

Pozzolanic and cementitious reactivity is increased with smaller particle size (Mehta and Monteiro, 2006). Ashes or cements with exceedingly large particles may not react completely and are less materially efficient. There are two common ways to quantify the reactivity of an ash or cement material based on its fineness: percent passing a particular sieve or Blaine surface area expressed as area per mass. Particles larger than 45 μm show little to no activity, while those smaller than 10 μm are highly active (Mehta and Malhotra, 2008). The Rawhide spray dryer ash was determined to have 8 percent retained by wet sieving according to ASTM C 430 – Fineness of Hydraulic Cement by the 45-μm (No. 325) Sieve. ASTM C 618 requires that the percent retained on the 45-mm sieve be less than 34 percent for fly ash used in concrete. This limit is rarely approached with U.S. fly ashes (Mehta and Malhotra, 2008). The Rawhide ash was also wet sieved on a 75-μm (No. 200) sieve resulting in 3 percent retained. Given the large size, the 3 percent of particles larger than 75 μm may never react completely (Mehta and Monteiro, 2006).

The analyst at BASF also performed microscopy on the SDA material. Figure 3.1 shows a photomicrograph of the Rawhide ash, prepared by the immersion method, and taken on a Zeiss petrographic microscope at 630X magnification (BASF, 2008). The glassy nature of the particles is clearly visible in this image. The dirty appearance of some of the particles (the large particle in the upper left-hand corner for instance) is common of high-lime fly ashes with surface coatings of alkali sulfates (Malhotra and Mehta, 2008). Note that all of the particles in the viewing area are smaller than the

12.7 μm scale with many appearing smaller than one μm. Considering this as a representative sample, this fly ash has a significant proportion of its particles under 10 μm, and should thus have a relatively high reactivity (Malhotra and Mehta, 2008). The very fine particle size is consistent with other reports of spray dryer ashes that were reviewed by EPRI (2007).

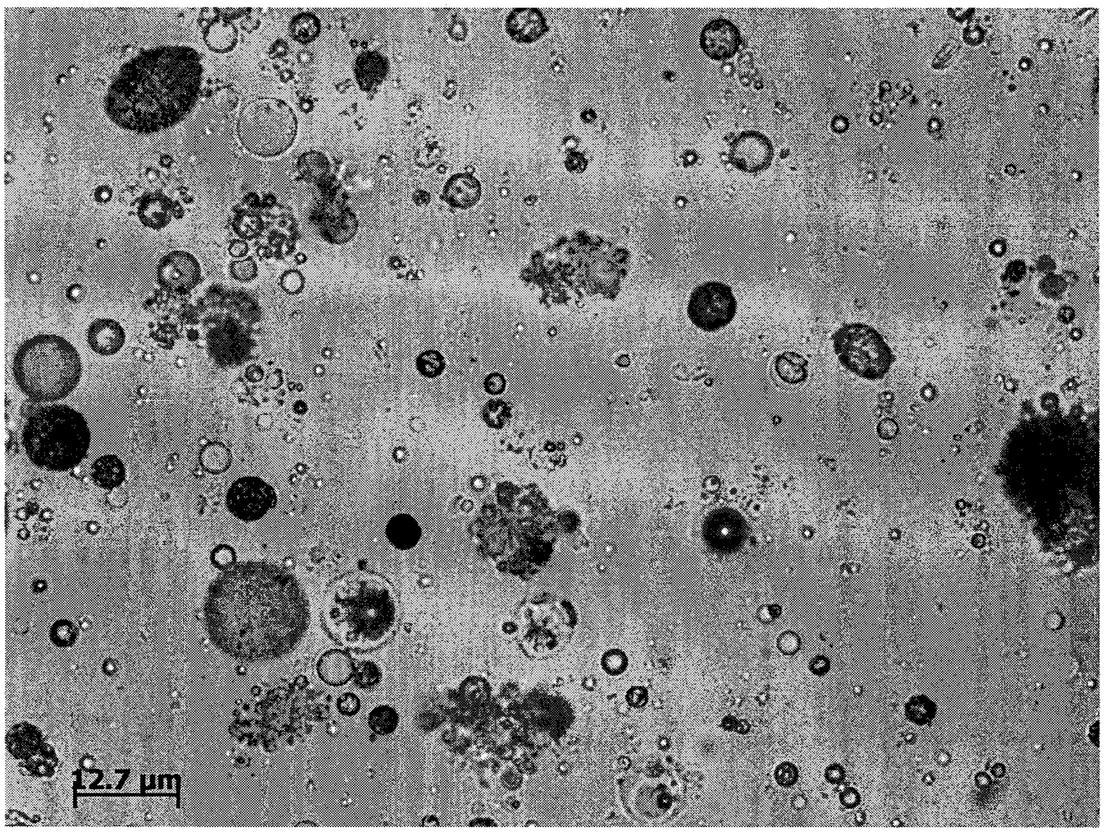


Figure 3.1. Photomicrograph of the SDA material from Rawhide Power Station, prepared by the immersion method, and taken on a Zeiss petrographic microscope at 630X magnification.

3.1.2 Sand

The sand used in the mortar mixes conformed to ASTM C 33. The result of a sieve analysis conducted according to ASTM C 33 is provided in Figure 3.2. ASTM C 778 – Standard Specification for Standard Sand uses slightly different parameters and a different range of sieves. This sand is commonly referred to as Ottowa sand and was not available for the tests conducted here. The moisture content of the sand was determined to be very dry (0.02 percent) according to the method specified by ASTM C 70.

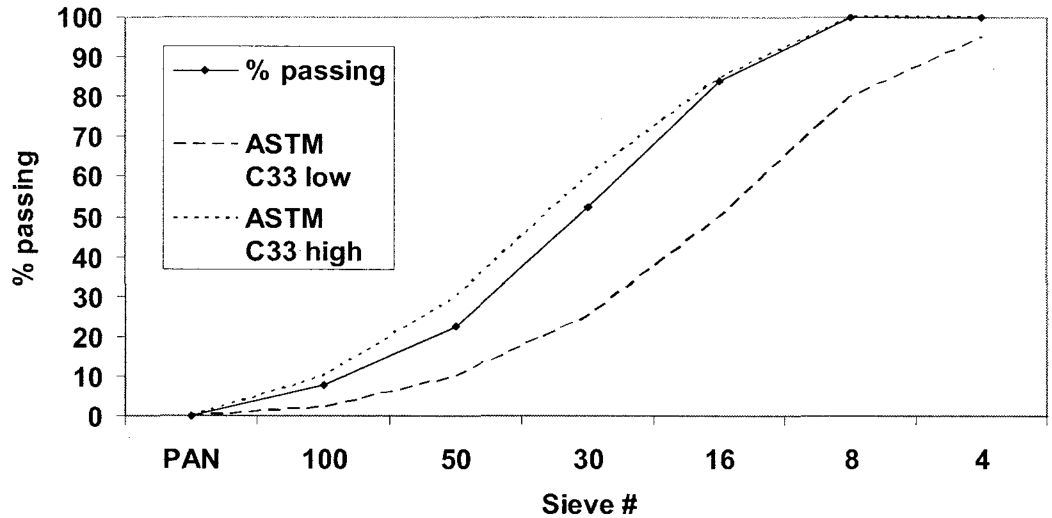


Figure 3.2. Sieve analysis for sand used in mortar.

3.1.3 Polymer Fibers

The polymer fibers used in this study (Figure 3.3) were obtained from, JaiTire, a used tire processing facility in Denver, CO that normally sends the fibers to a landfill (Choi, 2007). They represented a combination of polymers commonly used as tire reinforcement such as nylon, polyester and aramid with lengths distributed between approximately 2 mm and 30 mm. The steel wires usually present in most automotive tires were removed magnetically at early stages of the recycling process to be sold as scrap, and only an occasional stray was found in the fibers. The fibers were interspersed with rubber particles varying from fine dust to larger pieces less than 0.5 cm in dimension as well as raw chopped fibers that were still twisted together in cords. These recycled fibers were chosen for their compatibility with the theme of waste diversion and sustainable construction, which is a prime motivator for developing a cementitious material with high coal ash content. However, because they were not obtained from the original manufacturer, the specific composition and properties of these fibers is not well known. This lack of information is particularly apparent in the reporting of fiber fractions. The fiber fractions discussed throughout this dissertation are by mass, as without the density it was not possible to determine a volume fraction, which is how the percentage of fibers would typically be reported for proportioning purposes. The specific gravity of polymer reinforcing fibers varies from 0.9 for polypropylene to 1.16 for nylon to 1.44 for aramid fibers (Balaguru and Shah, 1992). Based on this range, a one-percent weight fraction translates to either 0.61 percent (assuming fiber specific gravity is 0.9) or 0.97 percent volume fraction (assuming fiber specific gravity is 1.44). Thus, the volume fractions can be considered to be approximately equal to the weight fractions reported if the specific gravity is taken as 1.44.

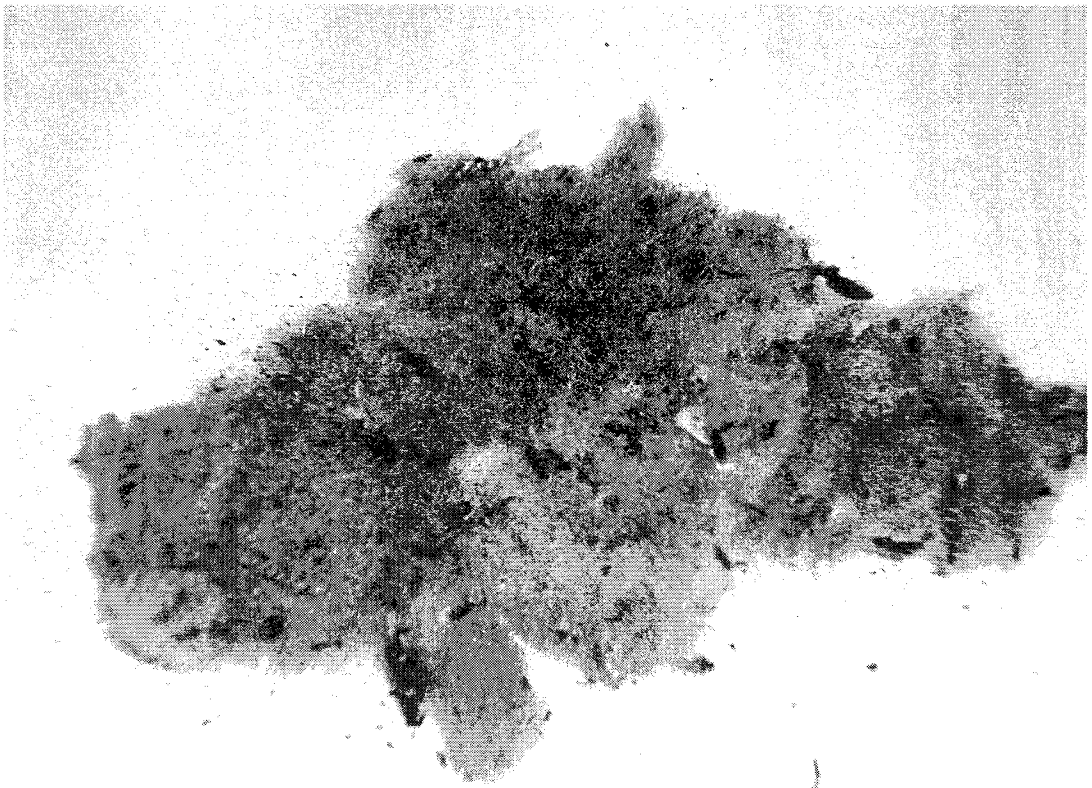


Figure 3.3. Polymer fibers resulting from the recycling of automobile tires used in this study. Note the presence of fibers still in twisted string and rubber particles interspersed.

3.1.4. Cement

ASTM C 150 – Standard Specification for Portland Cement provides the chemical, physical and mineralogical characteristics required of Portland cement. The cement types used in this study were I/II and III. Type I/II cement has traditional curing characteristics with less than 8 percent calcium aluminate to encourage sulfate resistance (recall that sulfates combine with calcium aluminate to produce ettringite). Type III cement has high early strength properties due to higher calcium aluminate content (less than 15 percent) and higher specific surface area (i.e. finer particles) compared to Type I/II cement. Type III cement was considered here to determine if the high early strength of the cement would improve the early strength properties of the cement-ash mix as suggested in Naik and Chun (2003). It was also assumed that the pozzolanic reactions of the ash would improve the later strength of mixes with Type III cement, which is normally lower than that for products made with Type I/II cement (Mehta and Monteiro, 2006). Cement was added in order to produce the traditional hydration products of CSH and CAH, but also to provide a source of hydrated lime to further react the pozzolanic compounds in the spray dryer ash.

3.1.5. Mixes

The mixes considered in this work are shown in Table 3.2. Variations in cement type (I/II or III), cement fraction (0, 5, 10, 15, or 20% by mass), and fiber fraction (0, 0.5, 1.0, 1.5, 2% by mass) were examined. Sand was added to each mix at a sand-to-cementitious materials ratio of one-to-one by mass. Previous work by researchers at Colorado State University with ash-only pastes had shown that a water-to-ash ratio of 0.4 was effective for producing both reasonable strength and good workability. Cross et al. (2008) reported that 0.2 and 0.23 water-ash ratios produced a slump of four to six inches, however attempts to create a workable mix at ratios less than 0.4 with the ash material investigated for this dissertation resulted in dry mixes that required excessive handling and packing to cast.

Table 3.2. Mix design proportions for the various compositions considered in this study.

Mix Number	Cement Type	Cement (mass % of ash plus cement)	Spray Dryer Ash (mass % of ash plus cement)	Sand (mass % of ash plus cement)	Water (mass % ash plus cement)	Fibers (% solids by mass)
1	---	0	100	100	40	0
2	---	0	100	100	40	0.5
3	III	5	95	100	40	0
4	III	10	90	100	40	0
5	III	15	85	100	40	0
6	III	20	80	100	40	0
7	I/II	5	95	100	40	0
8	I/II	10	90	100	40	0
9	I/II	15	84	100	40	0
10	I/II	20	80	100	40	0
11	III	5	95	100	40	0.5
12	III	10	90	100	40	0.5
13	III	15	85	100	40	0.5
14	III	20	80	100	40	0.5
15	I/II	5	95	100	40	0.5
16	I/II	10	90	100	40	0.5
17	I/II	15	84	100	40	0.5
18	I/II	20	80	100	40	0.5
19	I/II	10	90	100	40	1.0
20	I/II	10	90	100	40	1.5
21	I/II	10	90	100	40	2.0

ASTM C 305 – Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency requires that a planetary, rotary mixer be used for mixing mortars such as those tested here. Because such an apparatus was not available, a five-gallon plastic bucket was used along with a plaster mixing bit attached to a variable speed drill. The procedure for mixing mortars outlined in ASTM C 305 was followed approximately. For each mix, the following procedure was used. Components were measured into separate containers. Water was placed in a five-gallon bucket. Fibers, if any, were added, wetted and distributed as much as possible. Cement, if any, was added and mixed into solution. A third of the ash was added with a third of the sand and mixed until wetted with the drill. Another third of the ash and sand was added and mixed similarly. The final third of the ash and sand was added and the mix was stirred until a uniform consistency was achieved, usually no longer than two minutes.

For each mix, twelve 50-mm (2-in) cubes were cast to be tested in compression according to ASTM C 109 at 7, 14, 21, and 28 days in order to observe strength development over time. Six prisms with approximate dimensions 50 mm by 50 mm by 200 mm were cast to be tested in flexure according to ASTM C78 with a 150-mm span. The method of molding should be considered "alternative" according to ASTM C 109. Gloved fingers were used rather than a tamping rod and rounds of tamping suggested in ASTM C 109 were followed approximately. Cube and prism specimens were cast at the same time from the same mix and were placed in a curing room at approximately 90 percent relative humidity and 22 ^{o}C. Note that ASTM C 511 – Standard Specification for Mixing Rooms, Moist Cabinets, Moist Rooms, and Water Storage Tanks Used in the Testing of Hydraulic Cements and Concretes specifies that "the temperature of the air in the vicinity of the mixing slab, molds, and base plates shall be maintained at 23.0

+- 4.0 °C and at a relative humidity of not less than 50%" and "the temperature of the mixing water used to prepare cement paste and mortar specimens shall be 23.0 +- 2.0 °C." ASTM C 511 also states that "the atmosphere in a moist cabinet or moist room shall have a temperature of 23.0 +- 2.0 °C and a relative humidity of not less than 95%." Thus, the temperature in the moist room employed for this study complied with the standard, but the relative humidity was lower than the limit specified by approximately 5 percent relative humidity. The molds were stripped after one day and the specimens were stored in the curing room until testing.

3.2 Methods

3.2.1 Compression Testing Procedure

A MTS Universal Testing Machine with 267-kN capacity and hydraulic control was used and controlled with MTS TestStar software. Displacement control was used and a displacement rate of 0.5 mm/min was used to generate a load rate approximately between the 9 N/s and 1.8 kN/s specified in ASTM C 109. A fixed load platen was used on the bottom and a freely rotating load platen was used on top to ensure that the loading was evenly distributed.

Specimens without fibers failed catastrophically and the test was stopped soon after the peak load was reached. Some fiber-reinforced specimens were tested until they held approximately 20 percent of their peak load to examine the full stress-strain behavior. However, the testing of most reinforced specimens was stopped soon after they reached peak load. While no specification is available for testing the stiffness of mortars with

50-mm specimens, the stress-strain behavior of the cubes was analyzed and modulus of elasticity values were calculated using the chord method. At the very least, these results can provide relative stiffnesses between the various specimens. The actual stiffness value is not expected to correlate well with other published results as these are often determined using 150-mm diameter concrete cylinders per ASTM C 469 – Standard Test Method for Static Modulus of Elasticity and Poisson's Ratio of Concrete in Compression. Stiffness results were not desired when the experimental program was developed, but were found to be useful after the fact and are thus presented here despite the fact that the specimen shape is not intended for the purpose of determining Modulus of Elasticity.

3.2.2 Flexural Testing Procedure

Flexural testing of the specimens was conducted on beams with approximate dimensions 50 mm by 50 mm by 200 mm according to ASTM C 78 – Standard Test Method for Flexural Strength of Concrete (Using Simple Beam with Third-Point Loading). It should be noted that testing of mortars for flexural strength is outlined in ASTM C 348 – Standard Test Method for Flexural Strength of Hydraulic Cement Mortars and that fractured specimens from this testing can be tested for compressive strength according to ASTM C 349 - Standard Test Method for Compressive Strength of Hydraulic-Cement Mortars (Using Portions of Prisms Broken in Flexure). Given that metal molds conforming to ASTM C 348 were not available at the time of testing, ASTM C 78, with its more general approach and flexibility with respect to specimen dimensions, was used. A flexural specimen installed in the testing apparatus is shown in Figure 3.4.

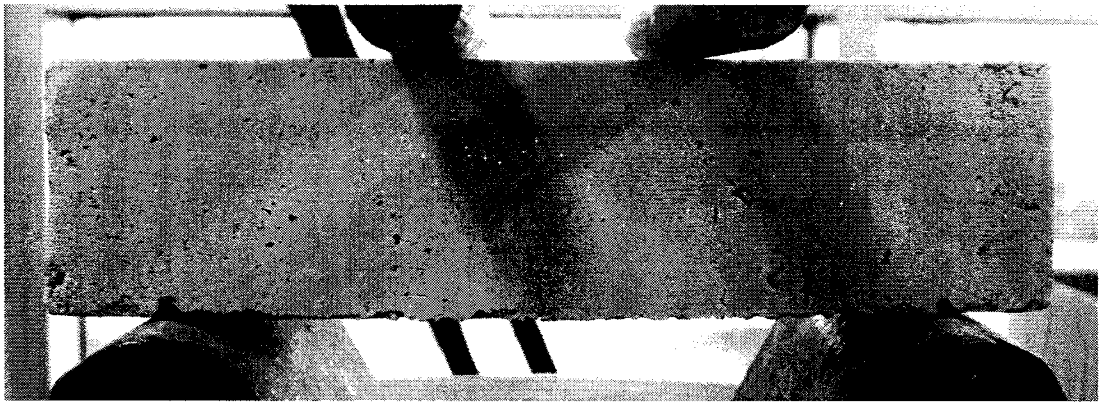


Figure 3.4. Flexural specimen under third point loading.

4. Results

This study investigated the influence of cement type, cement content, and fiber content on the compressive strength and stiffness, flexural strength, and qualitative characteristics of hydrated spray dryer ash from Rawhide Power Station. These results were considered in an effort to determine beneficial use applications for this widely available by-product. The quantitative results of 50-mm cubes in compression and 50-mm by 50-mm by 150-mm beams in flexure are presented below along with qualitative observations. Bar charts depicting average results with extreme values are provided in Appendix A. Each value provided in this chapter is an average of a 3-specimen sample. The results refer often to percentages of fiber or cement. These percentages are by mass with the fiber mass fraction being the mass of the fibers as a percentage of the mass of the solids (i.e. cementitious materials, fibers, and sand) and the cement fraction being the mass of the cement as a percentage of the mass of the total cementitious material (i.e. cement plus ash).

4.1 Compression Results

The results of testing in compression are provided in this section. First, the physical behavior of the specimens is discussed as it was observed during testing. Second, the stress-strain behavior of the hydrated ash materials in compression is examined with differences resulting from cement and fiber addition noted. Third, quantitative results of compression testing for strength are provided and analyzed with respect to varied cement type and fraction, strength development with time, and varied fiber mass fraction.

Fourth, the modulus of elasticity in compression is compared between specimens with varied cement and fiber mass fraction and trends are discussed.

4.1.1 Physical Behavior

Compression specimens without fibers exhibited traditional brittle failure modes with the Poisson effect and shear bond failure opening cracks within 30 degrees of vertical (Mehta and Monteiro, 2006). Material on the sides of specimens spalled in various amounts depending on location and fell away (Figure 4.1a). After failure, solid pyramids or cones of material remained; the material in contact with the load platens stayed mostly intact and the material in the middle section was generally disintegrated. When fibers were included, the failure was much more ductile. The fiber-reinforced specimens maintained their shape and, while cracks evolved as described above, the material did not fall away (Figure 4.1b).

(a) (b)

Figure 4.1. (a) Un-reinforced and (b) fiber-reinforced cube specimens after compression testing.

4.1.2 Stress-Strain Behavior

The stress-strain behavior of the compression specimens with and without fibers also demonstrates the improved ductility as a result of fiber inclusion. Figure 4.2 is an example of the stress-strain behavior of two specimens: one without fibers and one with one percent fiber mass fraction. The stress-strain behavior of the specimen without fibers is brittle; it is essentially linear to failure and falls rapidly after reaching the ultimate stress. There is some additional, albeit reduced, capacity beyond the ultimate stress, but the specimen undergoes a fairly rapid strain softening once ultimate failure has occurred. This is likely a result of continued consolidation of the now pulverized material rather than inherent integrity or strength. The specimen with one percent fiber mass fraction has a more ductile stress-strain behavior; there is a defined yield stress where the behavior deviates from linear and stiffness is reduced before the ultimate stress is reached. There is not a rapid reduction in capacity beyond the ultimate stress. Rather, the stress-strain curve is continuous and strain softening is more gradual as compared to the specimen without fibers. It appears in this figure that both the strength and stiffness of the specimen containing fibers are lower than those of the specimen without fibers, although this may be unique to these two specimens. Johnston (2001) notes that decreased compressive strength may result from fiber addition as a result of decreased consolidation of the matrix due to the presence of fibers. A more detailed examination of compressive strength and stiffness will be provided in sections 4.1.3 and 4.1.4, respectively.

Measures of toughness and ductility can be derived from stress-strain behavior. These quantities are especially important for fiber-reinforced brittle matrix composites as improvements in them are generally more pronounced and reliable than changes in strength or stiffness, which can be quite variable. Ductility is the tendency of a material to deform plastically past the elastic limit without fracture. It is generally quantified by measuring residual load at some deflection beyond first crack in reinforced brittle matrix composites. Toughness is measured based on the area under a stress-strain or load-deflection diagram up to a certain strain or stress level relative to the ultimate stress. Increases in toughness and ductility occur together although their magnitudes may differ. ASTM C 1018 - Standard Test Method for Flexural Toughness and First-Crack Strength of Fiber-Reinforced Concrete (Using Beam With Third-Point Loading) provides methods for quantifying ductility, but the testing conducted on the compression specimens was not carried to any consistent strain level as evidenced by the results shown in Figure 4.2. ASTM C 1018 was also withdrawn in 2006 due to lack of interest. Thus, discussions of toughness and ductility here will be approximate or qualitative.

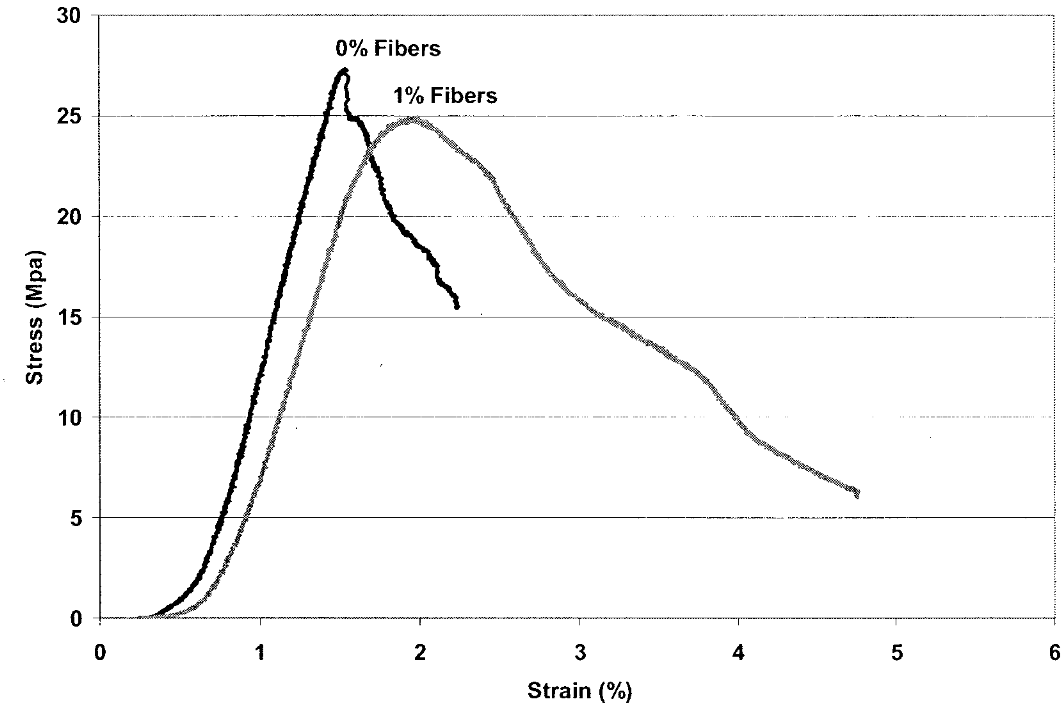


Figure 4.2. Stress-strain behavior in compression of cube specimens with 10% Type I/II cement and 0% or 1% fiber mass fraction at 28 days.

4.1.3 Compressive Strength

The results in the following subsections will address the compressive strength of hydrated spray dryer ash as it changes with varied Portland cement type and fraction, age, and varied fiber mass fraction. The results generally indicate the expected trends of increased strength with cure time and increased strength with added cement content, regardless of whether that cement is Type I/II or Type III. A more detailed analysis of these trends exposes variability in the results that makes it somewhat difficult to draw conclusions on all aspects of the material strength development and improvement with added cement or fibers.

The quality of the individual data sets is reasonably good. Variations in cube strengths within each sample set were acceptable with an average coefficient of variation of eight percent for cubes without fibers and nine percent for those with fibers. Coefficients of variation were rarely greater than 15 percent and approximately a third of the sample sets had coefficients of variation of less than five percent. Thus, the sample sets can be considered reliable as far as strength is concerned and are within precision limits recommended by ASTM C 109. However, trends between sets do not seem quite as consistent. Some trends are expected while others seem anomalous and may be related to variations in laboratory procedure or material non-homogeneity. In particular, sets with 0.5 percent fiber mass fraction and Type I/II cement (Table 4.2 and sets 15-18 in Table 3.2) exhibited illogical trends and were considered inconsistent when compared to other results. They should be thrown out in all cases, but are provided in the following results for completeness. A more detailed discussion is provided in each subsection below.

4.1.3.1 Compressive Strength with Varied Cement Type and Fraction

The average compressive strengths for the three-specimen samples with varied cement type and fraction are provided in Table 4.1 for specimens without fibers and Table 4.2 for specimens with 0.5 percent fibers. These results are plotted for comparison in Figure 4.3.

Table 4.1. Compressive strength (MPa) of specimens with varying cement additions and no fibers at 7, 14, 21, and 28 days.

Age (days)	0%	Type I/II Cement Fraction				Type III Cement Fraction			
		5%	10%	15%	20%	5%	10%	15%	20%
7	4.1	17.6	13.0	16.2	15.9	15.2	23.0	19.8	23.0
14	6.9	23.6	17.8	23.9	25.7	20.6	27.1	27.8	24.4
21	8.0	24.4	24.5	32.6	32.8	23.6	30.0	27.1	31.9
28	8.0	27.4	27.1	34.0	37.2	22.9	29.3	29.2	28.8

Table 4.2. Compressive strength (MPa) of specimens with varying cement additions and 0.5% fibers at 7, 14, 21, and 28 days.

Age (days)	0%	Type I/II Cement Fraction				Type III Cement Fraction			
		5%	10%	15%	20%	5%	10%	15%	20%
7	6.1	14.8	14.5	16.9	32.8	11.5	19.0	21.2	27.2
14	8.8	19.5	17.5	17.9	43.6	25.3	27.6	31.0	33.0
21	9.5	21.8	18.1	21.8	41.4	25.2	25.7	31.1	38.9
28	10.0	21.4	22.1	21.1	48.7	25.2	26.3	29.9	37.2

Examining the results to compare Type I/II and Type III cement additions proves difficult. Within this study, these results are the most plentiful in terms of number of specimens tested. However, between sets including fibers (0.5 percent fiber mass fraction and Type I/II cement, specifically) and sets without fibers, the results do not maintain their trends as cement fraction is varied (see Figure 4.3). As the creation of the identical sets with 0.5 percent fibers and without fibers was intended to validate the results produced by each, the fact that they show varying trends introduces some uncertainty into the results. This uncertainty might be explained by variable laboratory technique or non-homogeneous materials. Analyzing the samples without fibers (Figure 4.3a and 4.3b), expected trends emerge. At seven days, specimens with Type III cement added (except at 5 percent fraction) are indeed stronger. At 28 days, specimens with Type I/II cement added are stronger (except at 10 percent fraction). With 0.5 percent fiber mass fraction (Figure 4.3c and 4.3d), this trend is not nearly as clear with mixed results at seven days. Results at 28 days are unexpected, mostly on account of the poor Type I/II cement results. Type III cement-added specimens are stronger in every case except for the 20 percent cement fraction and the strength of the 20 percent Type I/II specimens here deviates so dramatically as to be considered anomalous.

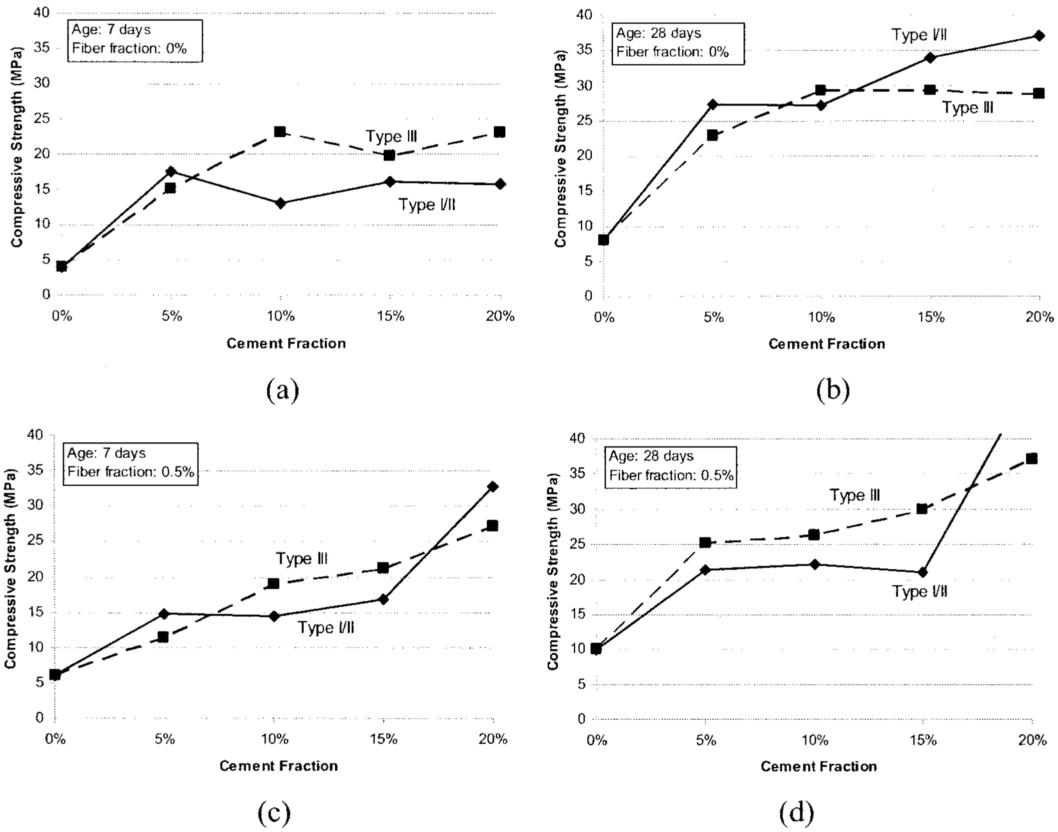


Figure 4.3. (a) 7-day and (b) 28-day compressive strength of specimens versus fraction of Type I/II and Type III cement with 0% fiber mass fraction and (c) 7-day and (d) 28-day strengths with 0.5% fiber mass fraction.

The trends in compressive strength versus cement fraction vary between specimens at various ages, casting some doubt on the validity of the trends at any particular age. As is traditional for cementitious material (especially concrete), the 28-day strength will be used to judge strengths of the materials. Figure 4.4 shows the increases in compressive strength as a factor of pure hydrated ash strength for the specimens with 0.5 percent fibers and without fibers at 28 days. Additions of Type I/II cement without fibers (Figure 4.3b, Table 4.1) show a significant increase in strength (factor of 2.9) with 5 percent cement addition, effectively no additional change with 10 percent addition and then additional improvements in strength with 15 and 20 percent cement added. Additions of

Type I/II cement with 0.5 percent fiber mass fraction show very different results (Figure 4.3d, Table 4.2). Specimens with 5, 10, and 15 percent cement added all have compressive strength of approximately 21 MPa, while the specimens with 20 percent added showed an average 28-day compressive strength of 49 MPa – a factor of 4.9 greater than the pure ash specimens. In fact, the strengths at all ages for the 20 percent cement added specimens are significantly higher than the corresponding strengths for specimens with less cement added. The Type I/II cement specimens without fibers are the most appropriate from which to draw conclusions because the results of specimens with 0.5 percent fiber mass fraction are generally more erratic and have poor trends throughout the study. In general, the addition of Type I/II cement has significant and increasingly positive effects on compressive strength as more is added. However, even a five-percent addition yields a more than three-fold increase in strength from the pure hydrated ash resulting in a material with strength sufficient to function in structural applications (27.4 MPa).

Five percent Type III cement added to specimens without fibers generates a factor of 2.9 increase compared to pure ash specimens (Figure 4.4). Additional cement further increases compressive strength from 5 percent added to 10 percent added, 15 percent does not appear to further improve strength, and strength decreases slightly with 20 percent cement added. Thus, the trend does not show consistent increases in strength with added Type III cement. As with the Type I/II cement results, the trend is different when 0.5 percent fibers are included. However, while the Type I/II results are highly variable and should be disregarded, a more likely trend emerges for the Type III cement with consistent increases in strength with added cement. In all cases, if a least squares fit is applied, there is a positive trend in compressive strength as cement fraction is increased. Given the overall variability of the data, however, the nature (e.g. linear, logarithmic, exponential, etc.) of this trend is uncertain.

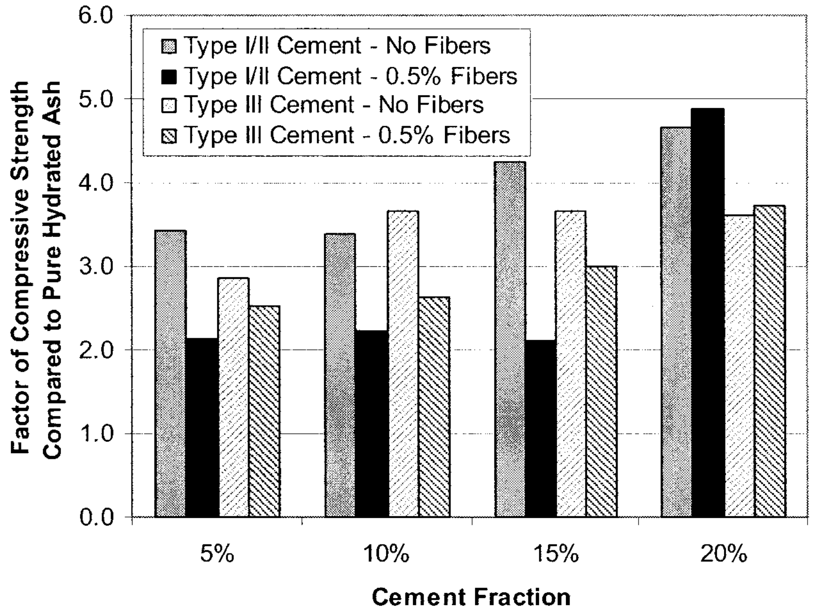


Figure 4.4. Improvements in 28-day compressive strength of specimens with added cement fraction compared to pure hydrated ash specimens.

Taken as a whole, the average of improvements in strength at all ages for specimens with any fraction (5 to 20 percent) of Type I/II cement and Type III cement compared to pure ash specimens is very close at a factor of 3.2. Even small fractions of cement added to a Rawhide ash mix confer a significant improvement in strength. It appears that these additions have diminishing returns with the first 5 percent generating the greatest relative strength gain (a factor of 3.4 for 5 percent Type I/II cement added compared to pure hydrated ash) and additional cement producing far smaller improvements. Perhaps the most significant finding here is that given these results, a 95 percent ash mortar could function in structural applications. Of course, further testing is required to rule out the potential for sulfate attack and quantify other important properties.

4.1.3.2 Compressive Strength Development with Age

The data in Tables 4.1 and 4.2 are plotted in Figure 4.5 to examine the strengthening of the specimens with age. In general, the expected rate of strengthening is visible although the rate tapers off in some cases. Certain specimens were weaker at 21 or 28 days. Figure 4.3 can be used to compare strength gain between seven and 28 days to observe the early strengthening effect of Type III cement when it is supplied in fractions of 10 percent and greater.

At 5 percent added, it appears that Type III cement does not have the effect it normally exhibits in a traditional concrete mix when compared to Type I/II cement; that of improving the early strength of the concrete. In fractions of 10 percent and greater, specimens with Type III cement are stronger than those with Type I/II cement at seven and 14 days. As would be expected, strengths of Type I/II cement-added specimens generally surpass Type III cement-added specimens at 21 days of age. It is interesting to note the degree to which the positive trend continues or not in Figure 4.5. The specimens including Type I/II cement and zero fiber mass fraction (Figure 4.5a) have a positive trend at nearly every age, while the others tend to flatten (Figure 4.5b, c, and d). Additional testing of these materials for longer periods to consider longer-term pozzolanic reactions would be important as these results indicate that in many cases, the materials may cease to gain additional strength after 14 or 21 days.

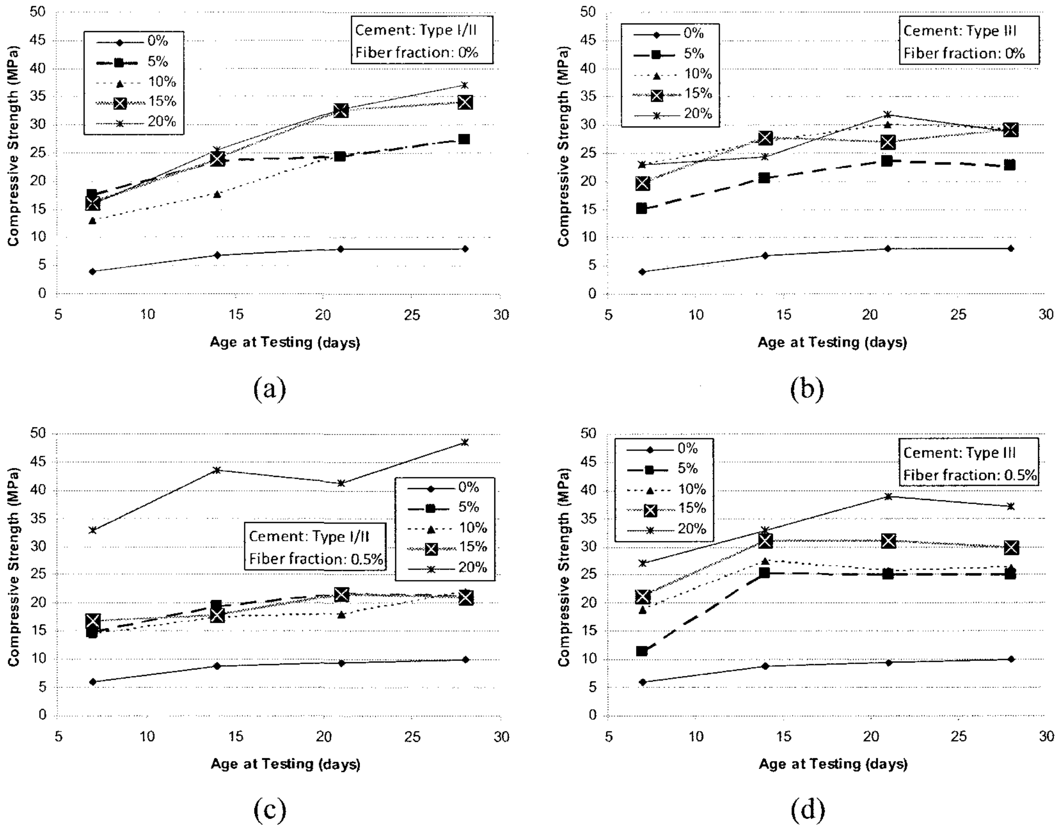


Figure 4.5. Compressive strength versus age: zero fiber mass fraction (a) Type I/II cement added and (b) Type III cement added; 0.5% fiber mass fraction (c) Type I/II cement added and (d) Type III cement added.

Figure 4.5 exposes some of the more inexplicable results that were obtained during this study that are again related to the specimens with 0.5 percent fiber mass fraction. While Figures 4.5a, b, and d show the general trend of increased strength with added cement fraction discussed in Section 4.1.3.1, Figure 4.4c shows the compressive strengths of specimens with 0.5 percent fiber mass fraction and Type I/II cement fractions of 5, 10, and 15 percent to be clustered together and significantly lower than those without fibers (Figure 4.5a). It also shows that the specimens with 20 percent cement fraction are twice as strong as any of the others in Figure 4.5c. Thus, again the specimens with Type I/II cement and 0.5 percent fiber mass fraction are difficult to explain and ought to be discarded in favor of the more reliable results.

4.1.3.3 Compressive Strength with Varied Fiber Fraction

The compressive strengths of specimens with 10 percent Type I/II cement and fiber mass fraction varied from zero to two percent are provided in Table 4.3 and plotted with respect to fiber mass fraction in Figure 4.6.

Table 4.3. Compressive strength (MPa) versus age for specimens with 10% Type I/II cement and varied fiber mass fraction. Specimens stronger than pure hydrated ash are in bold.

	Age (days)			
Fiber Fraction	7	14	21	28
0%	13.0	17.8	24.5	27.1
0.5%	**14.5**	17.5	18.1	22.1
1%	**16.3**	**23.7**	**29.3**	26.2
1.5%	**15.6**	**21.9**	**24.5**	26.4
2%	**13.1**	**18.5**	20.8	22.0

At early ages, it appears that the addition of some fibers is helpful, but over time the strength benefit of the fibers appears to be lost (note the bold results in Table 4.3). At seven days, any fraction of fibers appears to improve the compressive strength, while at 28 days the unreinforced specimens are the strongest, although fiber mass fractions of one and 1.5 percent are very close. These results follow a trend that is very consistent among differing materials in this study: weaker matrix materials are strengthened by the presence of the fibers while stronger matrix materials are weakened. Furthermore, there appears to be an optimal fiber mass fraction around one or 1.5 percent. The specimens with one percent fibers are stronger than the specimens with 1.5 percent fibers at most ages, and both outperform the specimens with two percent fibers at all ages. Again, the 0.5-percent specimens are weaker than would be expected, especially at later ages, and should be disregarded.

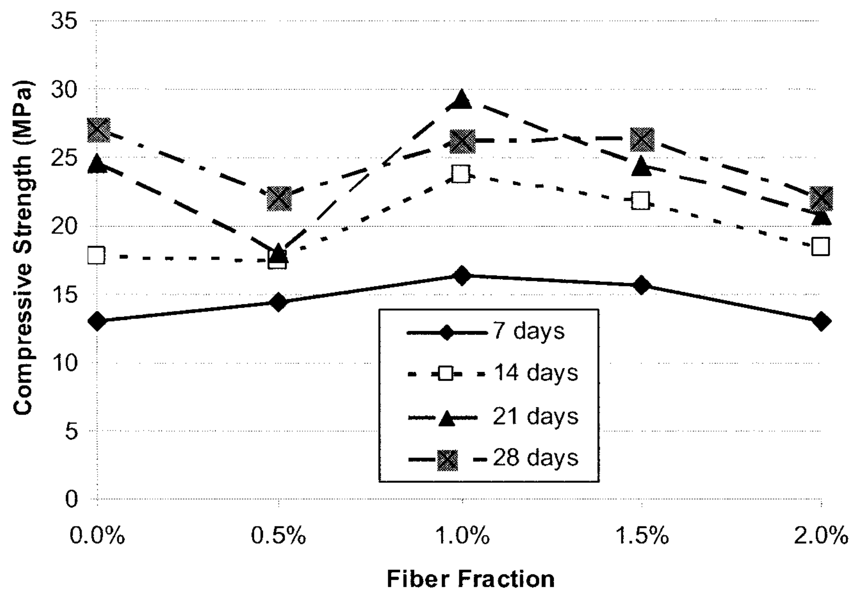


Figure 4.6. Compressive strength versus fiber mass fraction for specimens with 10% Type I/II cement at ages 7 through 28 days.

The fact that weaker materials appear to be strengthened and stronger materials weakened by the presence of the fibers can be explained by the relative strength and constitution of the matrix material at early and later ages compared to that of the fibers and the mechanism of failure prevented by fibers. Failure in brittle cementitious materials is initially based on the strength of the hydration products and later is related to voids and dislocations and the interfacial bonding between the hydration products and aggregates. At early ages, these hydration products are undeveloped, relatively weak, and relatively flexible. The binding properties of the fibers and their relatively uniform distribution in position and direction in a cube assist in crack bridging across shear planes. At later ages, when the hydration products have developed a stiffer and stronger structure the relatively weaker and more flexible fibers do not provide significant resistance to slipping along shear planes. When this is the case, the fibers are actually detrimental to the ultimate strength and stiffness of the composite material because they displace what could be additional hydration products and fill that space with a weaker and more flexible material. At this point, the rule of mixtures dictates that the composite material be degraded by the presence of the fibers and their lesser mechanical properties. In fact, most fiber-reinforced concrete research has indicated that the relatively weak reinforcement provided by polymer fibers such as nylon and polypropylene has little effect and can sometimes reduce strength by reducing consolidation and increasing entrapped air (Johnston, 2001; Balaguru and Shah, 1992).

The compressive strengths of hydrated ash without fibers and with 0.5 percent fiber mass fraction are given in Table 4.4. The behavior described above is visible in Table 4.4, where the weakest matrix material examined here, pure hydrated ash, is strengthened significantly at all ages by the presence of the fibers. It should be noted that the greatest strengthening occurs at seven days when the matrix material is the weakest, which further supports the identified trend.

Table 4.4. Compressive strength (MPa) of hydrated ash with and without fibers.

Age (days)	Fiber mass fraction 0.0%	Fiber mass fraction 0.5%	% difference
7	4.1	6.1	49%
14	6.9	8.8	27%
21	8.0	9.5	18%
28	8.0	10.0	25%

4.1.4 Compressive Stiffness

4.1.4.1 Compressive Stiffness with Varied Cement Type and Fraction

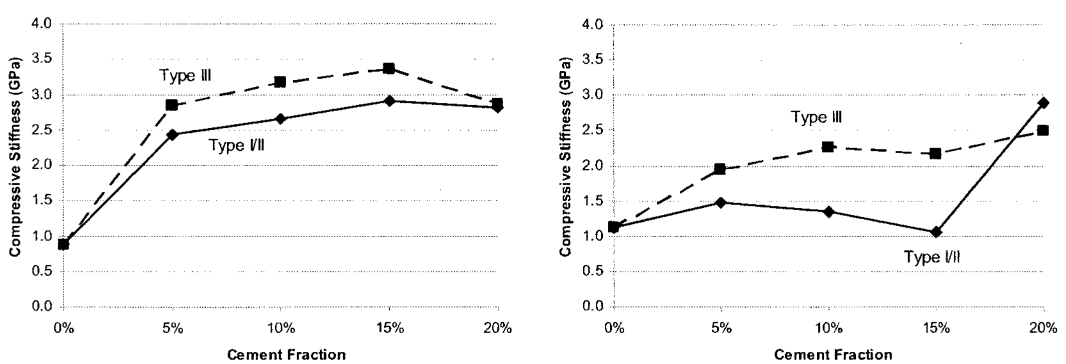
The modulus of elasticity of the test specimens was computed based on results from the compression testing. These results are shown in Tables 4.5 and 4.6 and the 28-day results are plotted in Figure 4.7. Because cube specimens, not standard 150-mm diameter cylinders, were used and the strain was calculated from displacement of the loading platen, these stiffness results represent only approximate values. However, given that all results presented here used the same method, they can be used to observe the relative effect resulting from the addition of Portland cement or fibers. The addition of cement clearly benefits the stiffness, producing stiffnesses of two to three times the stiffness observed for specimens made with spray dryer ash as the only binding agent. However, as with the compressive strength results there is a reasonably strong positive trend toward increased stiffness with increased cement fraction for the more reliable data (Figure 4.7a). The greatest increase in stiffness also comes with just 5 percent cement addition.

Table 4.5. Compressive stiffness (GPa) of specimens with varying cement additions and no fibers at 7, 14, 21, and 28 days.

Age (days)	0%	Type I/II Cement Fraction				Type III Cement Fraction			
		5%	10%	15%	20%	5%	10%	15%	20%
7	0.69	1.61	2.35	2.19	2.47	2.02	1.67	1.97	1.72
14	1.08	1.84	2.72	3.09	2.74	2.68	2.18	2.34	2.10
21	1.05	2.51	2.61	2.64	2.94	2.77	2.61	3.21	3.12
28	0.88	2.43	2.65	2.91	2.82	2.85	3.17	3.36	2.87

Table 4.6. Compressive stiffness (GPa) of specimens with varying cement additions and 0.5% fibers at 7, 14, 21, and 28 days.

Age (days)	0%	Type I/II Cement Fraction				Type III Cement Fraction			
		5%	10%	15%	20%	5%	10%	15%	20%
7	1.05	1.02	0.98	1.18	2.40	0.44	1.85	1.58	1.92
14	1.49	1.46	1.47	0.92	2.92	2.28	2.53	2.07	2.27
21	1.31	1.25	1.33	1.22	2.70	2.36	2.30	2.08	2.54
28	1.12	1.47	1.36	1.06	2.89	1.94	2.27	2.18	2.48



(a) (b)

Figure 4.7. 28-day compressive stiffness of specimens with varied cement fraction and (a) no fibers and (b) 0.5% fiber mass fraction.

The stiffnesses measured here are much lower compared to those predicted by the ACI Building Code and CEB-FIP Model Code equations relating modulus of elasticity to compressive strength (E_c = 25 to 30 GPa for f_c' = 27 MPa). This may be the result of a legitimately more flexible material, the fact that no large aggregates are used in this mix, or the use of cube specimens instead of large cylinders. Regardless, large-scale testing would be critical to using this material in structural applications and modification of traditional concrete design equations would be necessary.

4.1.4.2 Compressive Stiffness with Varied Fiber Fraction

Results indicating the effect of fiber addition on the compressive stiffness are shown in Table 4.7 and plotted in Figure 4.8. With the exception of the 0.5-percent fiber mass fraction specimens, these results show that the addition of fibers is of little benefit to a mix already containing cement and therefore already quite stiff. There appears to be very little advantage to fiber addition at early ages, but by 21 and 28 days the stiffness of specimens with fibers meets or slightly exceeds the stiffness of those without fibers. This is opposite the effect of fibers on compressive strength, where greater improvements were noted for younger weaker specimens including fibers. It appears that fiber addition in this particular matrix material slightly decreases strength and slightly improves stiffness at 28 days. Again, the 0.5 percent fiber results are well below the other values and do not fall into the otherwise well-established trend. These results should be considered anomalous and disregarded. While the addition of fibers does not influence stiffness to a significant degree, the fiber-reinforced specimens exhibited nearly equivalent stiffness, slightly decreased strength, and improved ductility and toughness as a result of the fiber addition in any amount. For these reasons alone a fiber-reinforced high-percentage ash material could be useful in design applications.

Table 4.7. Compressive stiffness (GPa) of specimens with 10% Type I/II cement and varied fiber mass fraction.

Age (days)	Fiber mass fraction				
	0%	0.5%	1%	1.5%	2%
7	2.35	0.98	2.03	1.72	1.84
14	2.72	1.47	2.47	2.80	2.24
21	2.61	1.33	2.97	2.60	2.82
28	2.65	1.36	2.70	2.74	2.86

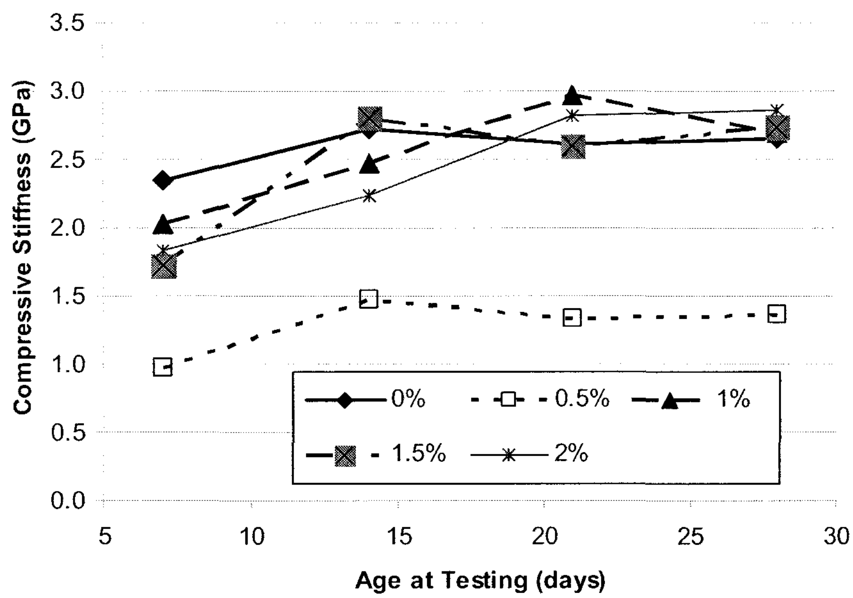


Figure 4.8. 28-day compressive stiffness for specimens with 10% Type I/II cement and varied fiber mass fraction.

The compressive stiffness of hydrated ash specimens with 0.5 percent fibers and without fibers is given in Table 4.8. Improved stiffness is noted at all ages as a result of fiber inclusion. It follows the same pattern of improvement as the compressive strength results of these specimens indicating that the fibers improve nearly all properties of this relatively weak and flexible matrix material.

Table 4.8. Compressive stiffness (GPa) of hydrated ash specimens with 0.5% fibers and without fibers.

Age (days)	Fiber mass fraction		% difference
	0.0%	0.5%	
7	0.69	1.05	53%
14	1.08	1.49	38%
21	1.05	1.31	25%
28	0.88	1.12	27%

4.2 Flexural Results

The results of testing in flexure are provided in this section. First, physical behavior is discussed as it was observed during testing. Second, the stress-strain behavior of the hydrated ash materials in flexure is examined with differences resulting from cement and fiber addition noted. Third, quantitative results of flexural testing for strength are provided and analyzed with respect to varied cement type and fraction and varied fiber mass fraction.

4.2.1 Physical Behavior

Flexural specimens without fibers exhibited brittle properties. Load was applied to specimens in third point bending, generating constant moment across the middle third of the specimen. The load was increased steadily and upon reaching the ultimate load a crack would appear and propagate rapidly leading to immediate collapse. Specimens with low fiber mass fraction would perform similarly. However, specimens with sufficient fiber content would crack in the tension region within the middle third of the span and lose capacity immediately only to regain it once the fibers in the cracked region were developed and carrying tension. If sufficient fibers were present, capacity would increase until a second peak load was reached. The crack would continue to propagate but capacity would fall slowly as it opened. This behavior is even more evident upon inspection of the stress-displacement behavior, which is discussed in the next section. Specimens with sufficient fiber mass fraction remained effectively intact upon removal from the testing apparatus. Figure 4.9 shows specimens without (left) and with (right) fiber reinforcing after ultimate load was reached.

(a) (b)

Figure 4.9. Flexural specimens (a) without and (b) with fiber-reinforcing upon reaching ultimate load.

4.2.2 Stress-Displacement Behavior

The stress-displacement properties of the specimens were highly dependent on their fiber mass fraction. Specimens with no or low fiber mass fraction would fail catastrophically at first cracking, while specimens with sufficient fiber mass fraction would lose some capacity upon cracking only to increase capacity (sometimes above the first crack load) until fibers debonded from the matrix material. The capacity of the specimen would drop slowly as the crack propagated and the fibers slipped within the matrix.

The effectiveness of fiber addition was highly dependent on the strength of the matrix material. Figure 4.10 shows the stress-displacement behavior of specimens with 10 percent Type I/II cement added and varying fiber mass fractions. The specimens with one percent and no fibers failed catastrophically at first cracking but had higher modulus of rupture, while the specimens with 1.5 or two percent fiber mass fraction had a lower modulus of rupture but greater ductility as evidenced by the secondary behavior visible in Figure 4.10.

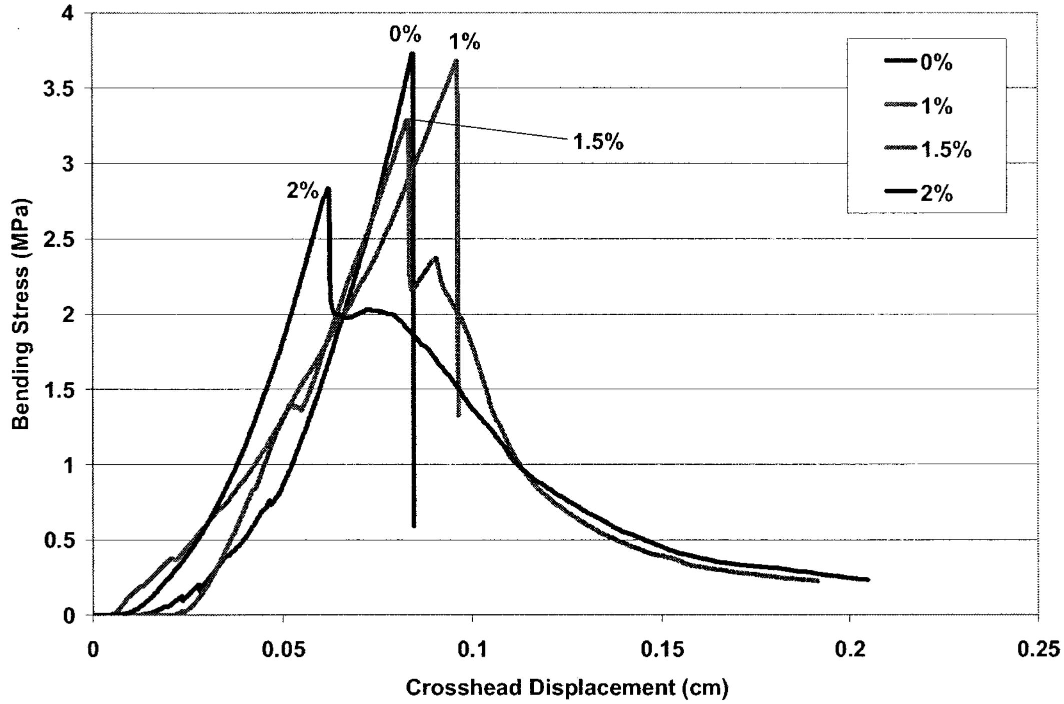


Figure 4.10. Stress versus crosshead displacement for flexural specimens with 10% cement addition and fiber mass fractions as labeled.

This behavior can be contrasted with the results in Figure 4.11 where the stress-displacement behavior of pure hydrated ash with 0.5 percent fibers and without fibers is shown. The average modulus of rupture for the beams containing fibers was 1.37 MPa, 11.5 percent less than the average for those without fibers: 1.54 MPa. However, only 0.5 percent fiber addition to the relatively weaker pure ash matrix provided sufficient reinforcing to observe the secondary behavior. More impressively, in two of the three samples shown, the secondary peak stress was greater than the first indicating good bonding between the fibers and ash matrix material. The moduli of rupture of beams with fibers were less than those without fibers in two of the three cases, which is similar to the behavior observed for the beams with cement added. It is also notable that the flexural stiffness of the beams containing fibers is decreased in Figure 4.11 (i.e. the slope of the stress-displacement curve is shallower), so in addition to the increased ductility and secondary behavior, a softer material is produced in general.

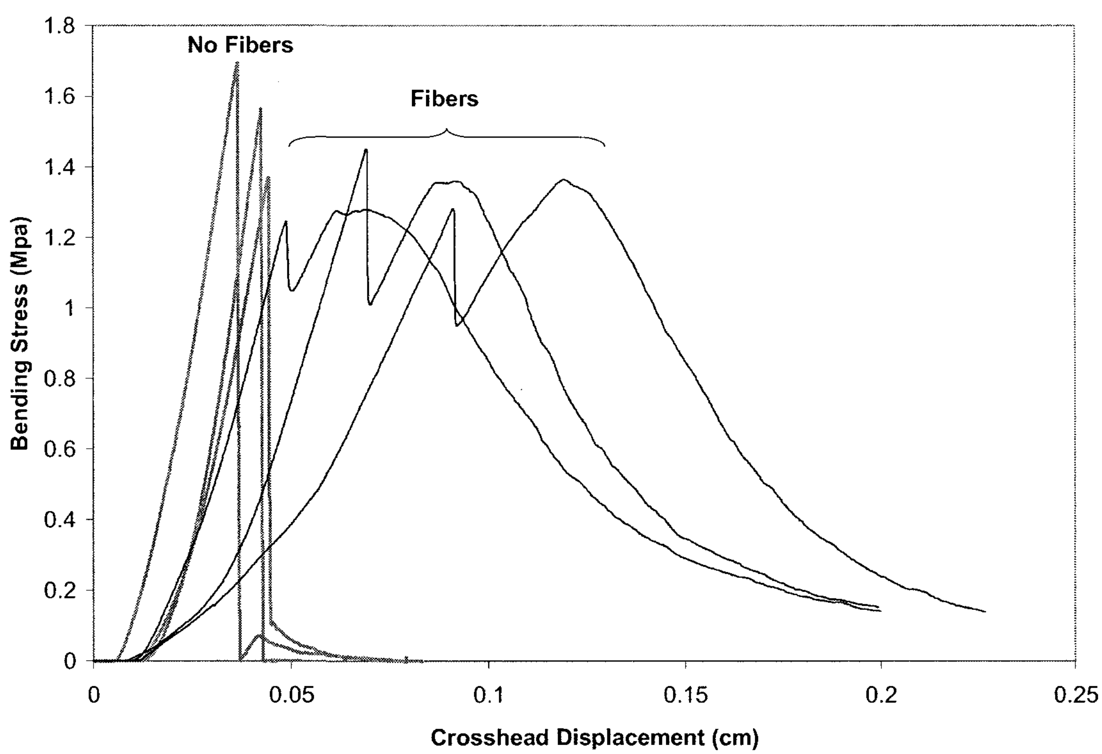


Figure 4.11. Bending stress versus crosshead displacement pure ash beams 28 days with 0.5% fibers and without fibers.

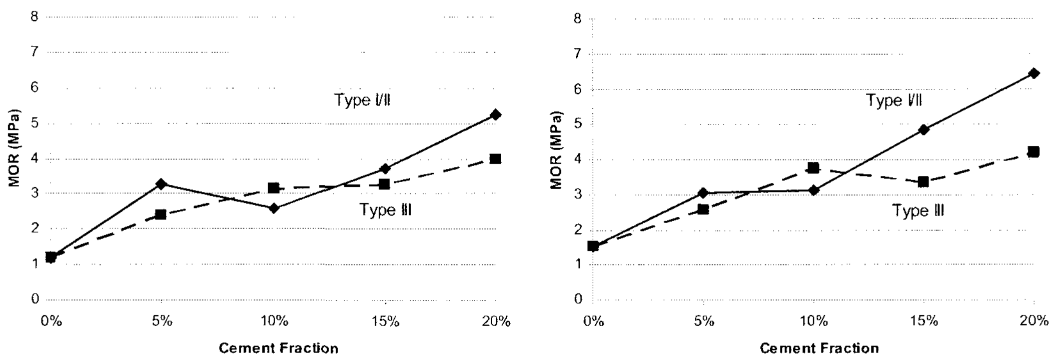
Based on the area under the curves in Figure 4.11, the toughness of the fiber-reinforced beams is improved by 50 percent up to first crack. Including the secondary behavior, the fiber-reinforced beams are approximately six times as tough as the specimens without fibers. The potential benefit of such improvements in toughness will be discussed further in the next chapter.

4.2.3 Flexural Strength

The moduli of rupture are given in Table 4.9 and plotted in Figure 4.12 for specimens with varied cement fraction. Similar to the compressive strength results, added cement results in increased bending strength. The only sample to violate this rule is the 15 percent Type III cement addition at 28 days. The modulus of rupture results do not show that Type III cement improves the early flexural strength. Type III cement-added specimens were stronger than Type I/II specimens at 10 percent added, but the Type I/II specimens show strength deviating from the expected trend at this fraction for some unknown reason. For all other cement fractions, Type I/II additions had greater moduli of rupture. Thus, there is nothing in these results to indicate that Type III cement improves early strength, but it should be noted that tests were not conducted at 7 days or earlier where this effect would be most pronounced.

Table 4.9. Modulus of rupture (MPa) at 14 and 28 days for specimens with varied cement fraction and no fibers.

Age (days)	Type I/II Cement Fraction					Type III Cement Fraction			
	0%	5%	10%	15%	20%	5%	10%	15%	20%
14	1.19	3.27	2.61	3.74	5.24	2.38	3.14	3.28	3.99
28	1.54	3.05	3.11	4.85	6.44	2.58	3.74	3.34	4.21



(a) (b)

Figure 4.12. (a) 14-day and (b) 28-day moduli of rupture versus cement fraction for specimens with no fibers.

The moduli of rupture are given in Table 4.10 and plotted in Figure 4.13 for flexural specimens with 10 percent Type I cement added and varied fiber mass fraction. Similar to the compression results reported in Section 4.1.3.3, there is a notable improvement in strength at a fiber mass fraction of one percent. However, as was shown in Figure 4.10, the secondary behavior with improved toughness and ductility was only visible for fiber mass fractions of 1.5 and two percent. Thus, there is a tradeoff to be considered with respect to strength or ductility when fiber mass fraction is chosen. The greatest improvement in strength was produced with one percent fiber mass fraction, but this set of specimens failed catastrophically in bending. The greatest improvement in ductility was had with two percent fiber mass fraction, but this set had a smaller modulus of rupture than the fiber-free set. The set with 1.5-percent fiber mass fraction showed improvements in both strength and toughness; it had a small increase in modulus of rupture along with the secondary behavior and ductility of the two-percent specimen, although to a lesser extent.

Table 4.10. Modulus of rupture (MPa) at 14 and 28 days for specimens with 10% Type I/II cement added and varied fiber mass fraction.

Age (days)	Fiber mass fraction			
	0%	1%	1.5%	2%
14	2.61	3.07	2.85	2.17
28	3.11	3.90	3.19	2.76

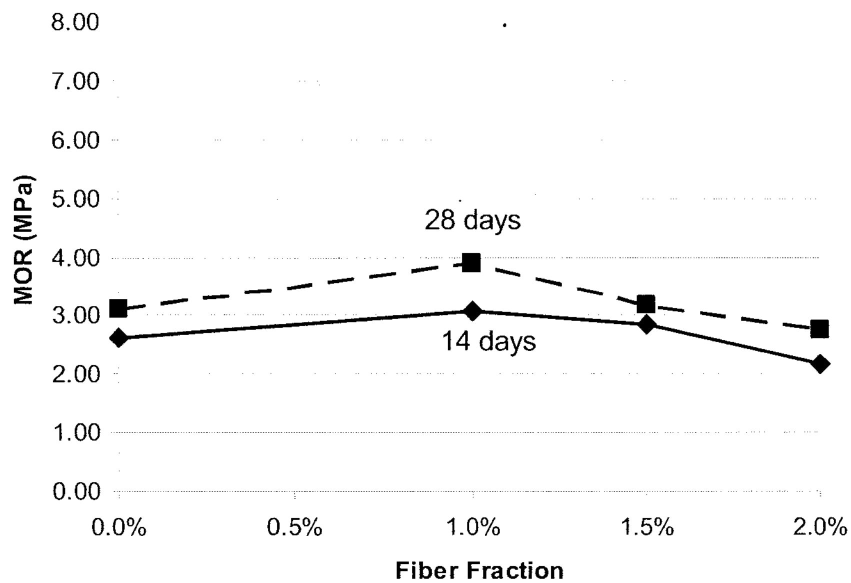


Figure 4.13. Modulus of rupture versus fiber mass fraction for specimens with 10% Type I/II cement at 14 and 28 days of age.

The moduli of rupture for hydrated ash with 0.5 percent fibers and without fibers is given in Table 4.11. It is interesting to note that the modulus of rupture is degraded at both 14 and 28 days with the addition of fibers in contrast to the increases in compressive strength reported for these mixes (Table 4.4). Again, these reductions in strength come with increased ductility and secondary behavior as shown in Figure 4.11. This is analogous to high-strength steel versus mild steel, where increased strength comes at the sacrifice of ductility. Like steel, this material can clearly be engineered for properties appropriate to different applications. A strong but more brittle material can be had or a tougher, more ductile material with reduced strength can be had depending on the fiber mass fraction included. Further investigation of varied cement additions with varied fiber mass fractions could result in a further optimized composite material.

Table 4.11. Modulus of rupture (MPa) at 14 and 18 days for hydrated ash specimens with 0.5% fibers and without fibers.

Age (days)	Fiber mass fraction		% difference
	0.0%	0.5%	
14	1.19	1.02	-15%
28	1.54	1.37	-11%

There is some question as to why any fiber mass fraction at all should result in *reduced* flexural strength as the fibers provide tension reinforcement in any amount and should therefore *increase* the flexural strength. Table 4.10 shows that the only reduced flexural strength comes with the two-percent fiber mass fraction and that the strength is reduced at both 14 and 28 days, so this result appears reliable, or at least consistent. Balaguru and Shah (1992) indicated that fibers carry with them entrapped air that can reduce the strength of the composite. Thus, it appears that with small fractions of fibers (up to 1.5 percent) the fibers succeed in reinforcing the brittle matrix in tension and improve the flexural strength. At the two percent fiber fraction, the fibers introduce sufficient entrapped air to overcome the beneficial effect of the fibers and reduce the strength of the composite.

4.3 Qualitative Observations

Several qualitative observations were made during the process of testing the hydrated ash specimens. The workability of the wet mix was good and finishing to a smooth surface was straightforward. There was a tendency for pure hydrated ash (without sand or cement) to be sticky, as noted by Malhotra and Mehta (1996). The addition of sand improved this condition as did increasing amounts of cement. No drying or shrinkage cracking was observed in the specimens upon demolding, which follows behavior noted by other researchers that fly ash inclusion in concrete mixes reduced such cracking. The hydrated ash specimens had a chalky finish, could be scratched easily, and absorbed water readily. If a specimen was dipped in water and then removed, it was observed that the surfaces of the cube would very quickly be dry to the touch because any surface water had been absorbed into the specimen. Both the chalky finish and rapid absorption indicate that for practical use some type of coating may be necessary. However, the chalky surface quality appeared to be reduced with additions of cement, even at the five-percent fraction, indicating that decreased permeability and increased durability and abrasion resistance might come with increased strength as cement is added. Because none of these properties except strength were quantified, this observation should be investigated in future research. It was observed that the fly ash cubes containing fibers made a dull sound likely associated with lower frequencies and high damping when dropped. This suggests that improved sound insulation might be achieved with these materials since the low density of the matrix and high-loss characteristics of the fibers contribute to the internal damping of the composite. Finally, the beams and cubes that contained fibers retained their shape after testing, while those without fibers fractured completely; the cubes were ultimately pulverized while the beams broke in half. Thus, any incidental cracking in the fiber-reinforced material would not necessarily lead to crack propagation or immediate loss of capacity: a useful quality in many cases.

5. Discussion

The discussion presented below will consider numerous aspects of the spray dryer ash that was studied here. First, a summary of the work performed and substantive conclusions will be given. Second, life cycle considerations will be discussed and used to support a case for increased use of spray dryer ash in the built environment. Third, the potential will be evaluated for the materials developed and tested in this study to be used in civil and structural engineering applications. Fourth, the potential will be considered for the Rawhide Power Station spray dryer ash to be used in other engineering applications as suggested in the literature and supported by the test results presented here. Fifth, barriers to implementation of spray dryer ash in beneficial use applications will be presented. Finally, suggestions for future research will be made based on this discussion.

5.1 Summary and Conclusions

This dissertation described results of an ongoing project to evaluate the potential for using spray dryer ash and recycled tire fibers to provide a more sustainable alternative to traditional Portland-cement-based materials. Based on these results, the material investigated here has good potential for beneficial use. The material considered in this study has the added benefit that aggregate use is minimal and may even be unnecessary, which allows for higher-volume use of spray dryer ash and reduced natural resource extraction for aggregates. Before this material can be routinely used, continued development considering, for example, the use of other recycled or downcycled aggregate materials, long term durability, and handling characteristics is necessary. Based on the results of this work, materials consisting solely or primarily of spray dryer ash have the potential to be used as structural materials or in architectural applications where low-strength materials are appropriate.

The strengths and stiffnesses of pure ash mortars showed significant improvement with as little as 5 percent addition of Portland cement and were sufficient for general use concrete applications. Both Type I/II and Type III cements were found to be effective. The Type III cement helped the early strengths to some extent, while the Type I/II cement produced higher later strengths, especially at 28 days. The addition of any amount of cement 5 percent or greater eliminated the concern about the chalky finish associated with the pure hydrated ash specimens. It also improved the workability over the pure hydrated ash mortar, as the ash-only mixes tended to be sticky which made finishing somewhat difficult.

5.1.1 Compressive Behavior

The mortars tested here consisted of hydrated spray dryer ash with a water-to-cementitious materials ratio of 0.4 and varying fractions of Type I/II and III cements and/or recycled polymer fibers. Pure hydrated ash mortar had a 28-day compressive strength of 8.0 MPa and modulus of elasticity of 0.88 GPa. These properties were improved by adding either recycled polymer fibers or small fractions of Portland cement.

Adding 0.5 percent fibers by mass of the solids to a pure ash mortar improved the compressive strength by a factor of 1.25 to 10.0 MPa and significantly improved the ductility and toughness of the final product. The modulus of elasticity was also improved by 27 percent up to 1.12 GPa. While fiber fractions beyond 0.5 percent were not considered for the pure hydrated ash, the addition of fibers clearly improves all aspects of the hardened product including compressive strength, stiffness and toughness. This result was unique to the hydrated ash without cement and represents a synergy of the ash and fibers that ought to be exploited in some sort of low-strength cement-free application such as wallboard.

Adding five percent Type I/II Portland cement by mass of cementitious material improved the compressive strength by a factor of 3.4 to 27.4 MPa, which is a strength commonly used for structural concrete. Stiffness was improved by a factor of 2.74 to 2.43 GPa. Increased fractions of Portland cement resulted in increased compressive strength as well as stiffness, however the trend is not linear and the first five percent added cement was the most effective. Portland cement should be recognized as a highly effective activator for the hydrated ash, given the significant strength and stiffness gains associated with very small amounts added.

Adding both 10 percent Type I/II Portland cement and polymer fibers resulted in a material with significantly improved compressive strength (26.4 MPa), stiffness (2.74 GPa testing 50-mm cube), and toughness that has potential for use in a wide range of applications including structural ones. The fraction of fibers included in this material was found to be most beneficial in the 1 to 1.5 mass percent range. It is at this inclusion rate that the compressive strength and stiffness were both slightly improved. In general, the fibers had little to do with any improved properties for these specimens besides increasing their toughness. The improvements in strength compared to the fiber-free specimens were within 3 percent if they occurred at all, and improvements in stiffness were within 8 percent.

The ACI Building Code and the European CEB-FIP Model Code (1990) supply equations for estimating the modulus of elasticity of structural concrete. A normal-weight 27-MPa concrete should have a modulus of elasticity of 25 to 30 GPa, roughly ten times that of the mortars tested in this study. It should be noted again that the modulus of elasticity was determined for 50-mm cube specimens rather than standard 150-mm diameter cylinders. The impact of a more flexible but equally strong material on reinforced concrete design is intriguing. The material effectively shows similar strength to traditional concrete with approximately one-tenth the stiffness. This means the failure strain is approximately ten times that of traditional concrete making for a more deformable and thus more ductile member if reinforced properly. Given that the density of this material is less than traditional concrete as well, a novel design problem results with members having smaller dead loads and more flexible characteristics. This discrepancy in stiffness should be reevaluated using 150-mm diameter cylinders under the assumption that the 50-mm cubes do not provide a realistic, or at least comparable, measure of compressive stiffness.

It was determined that fiber inclusion in a relatively weak matrix material like the pure hydrated ash or mixes with Portland cement at early ages was most effective at improving compressive strength, while fiber inclusions in stronger matrix materials such as those with higher Portland cement contents at later ages could be detrimental to both strength and stiffness. This is explained by the relative strength and stiffness of the fibers and the fact that in a weak matrix they function effectively as a reinforcement to bridge cracks and prevent shear failure modes, while in a strong matrix their relatively weak properties and propensity for entrapping air are detrimental to the overall performance of the composite. The strengthening observed in the pure hydrated ash mortar may be the result of the weaker and less stiff matrix being reinforced by fibers that are relatively stiffer and thus able to reinforce the matrix prior to cracking. Once the matrix itself is stronger and stiffer, as is the case in the mortars with added cement, the fibers have a detrimental effect until after cracking has occurred and the fibers deform sufficiently to carry load. These results are consistent with the highly variable results for fiber reinforced concrete reported by other authors and summarized by Johnston (2001). The combination of brittle matrix material and fibers requires careful selection of both and the properties of the composite material should be researched more exhaustively than they have been here prior to any practical application. However, the composite materials considered here have the potential for use in many applications as they are, which will be discussed further below.

5.1.2 Flexural Behavior

There were unique differences in the effect of fiber and cement inclusion on the hydrated spray dryer ash properties in bending compared to compression. In general, flexural strength was improved via the addition of Type I/II or Type III Portland cement.

Ductility and toughness were improved via the addition of fibers. However, the effect of fiber inclusion on flexural strength was more variable.

Additions of fibers to the pure hydrated ash tended to degrade the flexural strength and stiffness while dramatically improving the toughness. With the stronger matrix material (10 percent Type I/II cement plus ash), the fibers improved the flexural strength at one and 1.5-percent fractions and degraded it at the two-percent fraction (Table 4.10). While the improvements in compressive strength were associated with reinforcing shear-dominated failure modes where the fibers were somewhat helpful, the fibers are less effective when the specimen is stressed in direct tension. Given that the one-percent fraction was not sufficient to allow for secondary load-deflection behavior and improved toughness, the 1.5-percent fraction was determined to be optimal. The mechanism that governs whether fibers improve or degrade the flexural strength is a complex one. Given that the fibers are relatively weak and flexible compared to the matrix they require large strains to assist in carrying load. This usually means that they are engaged after first crack and provide little benefit beforehand. While one percent fiber fraction does not provide enough polymer material to carry load beyond first crack, it does improve the modulus of rupture. Larger percentages bring with them entrapped air that reduces the relative density of the matrix material and can serve to degrade the strength even while the fibers improve the toughness. Thus, an optimum fiber fraction appears to exist where the beneficial effect of the fibers is not adversely impacted by the presence of the entrapped air.

5.2 Life Cycle Considerations

Based on the literature reviewed concerning LCA of concrete, life cycle benefits increase with increased Portland cement and raw material replacement. Thus, a hierarchy of structural products emerges based on their relative capacity to offset Portland cement and aggregate. Aggregate-free pure hydrated ash material is the ideal, or pure ash as a binder mixed with recycled aggregates such as recycled concrete or crushed post-consumer glass. A pure ash binder that replaces 100-percent of the Portland cement in a given concrete is an excellent alternative. Replacement of Portland cement in already efficient structural forms like concrete masonry units is effective. Finally, partial replacement of Portland cement in a given concrete mix can offset a significant portion of the most impactful portion of the product and perhaps provides the greatest opportunity for achieving a product with performance that is equivalent to or substantially better than a pure Portland cement concrete. While this has clearly been the focus of most "mineral admixture" research in the past, greater awareness of climate change and other environmental issues necessitates a more aggressive approach to produce concrete and concrete products higher up in this hierarchy. The effective utilization of self-cementing products like spray dry absorber material as demonstrated by the research reported here offers a very good opportunity to make such aggressive goals a reality.

5.3 Beneficial Use Applications

The are many beneficial use applications for spray dryer ash aside from those proposed above that have been suggested in the literature. EPRI (2007) outlined the potential applications for SDA materials based on opportunities implied by previous work with the material. High-potential applications included mining applications and cementitious products: masonry, flowable fill, and synthetic aggregate. Moderate-potential applications included cement replacement in concrete, engineered fills and embankments, agriculture, soil stabilization, and wet FGD sorbent. Low-potential applications included binders, cement feedstock, hazardous waste fixating agent, artificial reef material, mineral wool feedstock, sulfuric acid production, and wallboard. The research conducted here supports the use of SDA material in masonry, flowable fills, synthetic aggregate, engineered fills and embankments, hydraulic cement binders, and wallboard. The most effective uses for the material investigated here as indicated by the life-cycle hierarchy in section 5.2 will be described below.

5.3.1 Concrete Applications

28-MPa concrete is used regularly in foundations, pavement, bridge decks, columns and beams. Based on compressive strength and stiffness alone, numerous mixes investigated here may have potential for these applications. The numerous other properties that would require investigation prior to use in structural applications will be outlined in the Future Work section.

5.3.2 Hydraulic Cement Binder

ASTM C 1157 – Standard Performance Specification for Hydraulic Cement states that it "covers hydraulic cements for both general and special applications. This is a specification giving performance requirements. There are no restrictions on the composition of the cement or its constituents." Based on its definition, this specification opens the way for blended cements with high-volume ash contents to be developed and enter the market, especially those that are otherwise limited by prescriptive standards like ASTM C 618. A blended cement incorporating SDA material could be brought to market so long as it met the performance requirements of ASTM C 1157. The results of this work support the growing agreement that spray dryer ash, despite its variations in quality, can be used successfully as part of a hydraulic cement system. Further, these preliminary results indicate that the spray dryer ash from Rawhide Power Station has properties sufficient for use in a blended hydraulic cement. More specifically, based on the results presented here, a cement conforming to ASTM C 1157 standards containing at least 95 percent Rawhide ash could be developed and marketed as a GU (general use) or MH (moderate heat of hydration) cement. The compressive strength required for GU (general use) cements under ASTM C 1157 is 28.0 MPa and for MH (moderate heat of hydration) cements is 22.0 MPa. There is substantial research supporting blended cements with Class C fly ash, some include spray dryer ash (Wu and Naik, 2002, 2003; EPRI, 2009), and many include chemical activation with alkali solutions to improve performance, which is an option that was not considered here, but one that warrants further investigation. Reports are published that show such fly ash based blended cements have slightly improved resistance to sulfate attack and alkali-silica reaction compared to Type I Portland cement (Wu and Naik, 2003). It is uncertain how SDA material would behave in this application and if the higher levels of sulfur would be a detriment.

5.3.3 Masonry

Liu et al. (2005) have worked extensively with Class C fly ash to produce bricks. Their process consists of mixing water and fly ash with admixtures and fibers and putting the mixture in a mold under 6.9 MPa or more pressure and curing for two weeks in a moist environment. Kumar (2002) proposed fly ash-gypsum bricks for low-cost housing in India. Properties of the materials investigated here could meet the requirements for many masonry applications without additional temperature or pressure. Table 5.1 lists the appropriate ASTM standards regarding brick and masonry units, the compressive strength requirements of the specification, and the mixes investigated here that would satisfy those requirements. Most of these standards also have absorption and density requirements that would need to be investigated. However, ASTM C 129 – Nonloadbearing Concrete Masonry Units requires the lowest compressive strength and has no requirements for absorption and density. Even the pure ash mortar tested here would satisfy the requirements of this specification. Bricks produced from spray dryer ash would have the benefits outlined by Liu (high dimensional tolerance, lower weight than tradition bricks, improved insulation properties) with the added simplicity of manufacturing without pressure. However, there is a life-cycle tradeoff to be considered: 5 percent cement versus 6.9 MPa pressure required to manufacture.

Rawhide Power Station spray dryer ash is already used to offset 35 percent of the cement in architectural block manufactured on the Front Range of Colorado. Architectural block strengths (among other properties like absorption and dimensional stability) must comply with ASTM C 90. The required strengths for CMUs are relatively low at 13.1 MPa and could be met by any of the specimens incorporating just five percent Portland cement.

Table 5.1. ASTM standard specifications concerning concrete brick and masonry units, compressive strength requirements, and appropriate mixes.

ASTM Standard	Compressive Strength Requirement	Appropriate mix(es) investigated here
C 55 – Concrete Building Brick	17.2 MPa	Specimens with 5% or more Type I/II or III cement added Specimens with 10% Type I/II cement with any fiber fraction
C 90 – Loadbearing Concrete Masonry Units	13.1 MPa	Specimens with 5% or more Type I/II or III cement added Specimens with 10% Type I/II cement with any fiber fraction
C 129 – Nonloadbearing Concrete Masonry Units	4.14 MPa	Pure hydrated ash mortar with or without fibers and any specimens with cement and/or fibers added
C 1634 – Concrete Facing Brick	24.1 MPa	5% or more Type I/II cement added 10% or more Type III cement added Specimens with 10% Type I/II cement and 1% or 1.5% fiber fraction
C 1319 – Concrete Grid Paving Units	35 MPa	None - further development required
C 902 – Pedestrian and Light Traffic Paving Brick	55.2 MPa	None - further development required

5.3.4 Other Applications

Based on the other notable properties of the materials studied here, including low density, sound damping characteristics, and thermal properties as investigated by Choi (2007), there are numerous other potentially high-value applications for this material such as cement board, wall board, and double floor plates. The moderate strength and toughness of the fiber-reinforced cement-ash material suggests possible use as panels for a variety of applications like cabinetry, furniture products, or structural cladding.

Based on the good workability and strength exhibited by the hydrated ash materials, potential applications include flooring mastic, interior or exterior plaster, grout, and controlled low-strength materials. Given the compressive strength of the pure hydrated ash without fibers (8 MPa), there is excellent potential for use as a flowable fill, or controlled low-strength material (CLSM). The maximum strength for CLSM is 8 MPa, but most fills are designed for lower strengths to facilitate excavation. Given that a relatively low water-ash ratio was used in the specimens achieving 8 MPa, higher water-ash ratios would result in a more workable product with necessarily lower strength. Concerns exist regarding potential expansion due to ettringite formation, so further investigation is required for this application (EPRI, 2007). There is a potential landscaping application in light-traffic pedestrian pathways that require only moderate durability. Given the absorption characteristics of the pure hydrated ash, there is potential for use as a pervious pavement that would allow for groundwater infiltration as well as a pedestrian or light traffic surface. Although the material is likely not strong enough to withstand freeze-thaw cycles under saturated conditions it would probably be inexpensive and available enough to be reapplied at frequent intervals. The benefit of increased material beneficial use would have to be weighed against decreased durability compared to another product. A life cycle analysis and costing would likely oppose this application.

5.4 Barriers to Implementation

The barriers to implementation of SDA are varied and many, but generally fall into technical, environmental and economic categories.

5.4.1 Technical Barriers

Technical barriers depend on the potential application, but for the materials investigated here the most significant potential problems are long term performance and durability issues associated with sulfate attack. Further testing of these materials along with greater understanding of the mechanisms and precursors of sulfate attack is critical to overcoming this obstacle. Meaningful metrics for the physical, chemical and mineralogical characterization of coal ash are important to allow for effective technology transfer in the literature and accurate description of the ash-cement hydration products resulting from well-understood materials. The variability of ash from a given plant due to inherent material and process characteristics (noted for the RPS ash in the Experimentation chapter) is a significant barrier and requires that statistical descriptions of ash materials and their products be developed. Coal ash also varies from plant to plant due to variations in coal and SDA systems, which requires an expansion of the scope of statistical analysis to describe the variations in the greater coal ash producing community. Inconsistent terminology in the literature makes review and comparison difficult. ASTM E2201 – Standard Language for Coal Combustion Products provides appropriate language to describe products and processes associated with CCBs. The relative lack of extensive and conclusive research related to coal combustion by-products hampers efforts to promote CCB beneficial use. Well-planned and executed research should be funded and conducted across a wide geographic area to better understand the mechanisms and benefits of CCB beneficial use. Existing guidelines concerning beneficial CCB use are dependent on limited research and consistently suggest further study. Hence, further research will also put good information in the hands of decision makers and practitioners.

The limited life cycle data and tools available to analyze coal ash and traditional materials make comparison difficult. Further development in this arena will be critical to further quantifying environmental costs and placing them on equal footing with economic considerations. The performance-based standard ASTM 1157 has done much to alleviate the barriers imposed by prescriptive standards and specifications that disqualify ashes based on certain chemical or physical characteristics that may not necessarily limit their beneficial use. Further development of safe and effective performance-based standards will move the industry and society forward.

5.4.2 Environmental Barriers

Reiner (2007) notes that many of the perceived environmental risks of using fly ash in the built environment have been addressed, including radioactivity, inhalation, and leaching risks. It is widely noted that the heavy metal compounds and radioactive elements in fly ash exist at levels similar to soils and traditional building materials like brick. These levels of exposure are background levels encountered in everyday life and are deemed safe (EPA, 2008).

Environmental barriers that exist or will be problematic in the future include the potential for hazardous material designation for fly ash and related substances given recent high-profile events like the fly ash slurry spill at the Tennessee Valley Authority's Kingston Fossil Plant in 2008 (Eilperin, 2009). While this particular fly ash spill necessitates stricter regulations regarding ash disposal and storage methods, it should not be used to vilify coal ash as a dangerous industrial by-product. Changing emissions standards are likely to cause process changes that result in ashes with modified characteristics or potentially new CCBs altogether. Continued research is critical to finding beneficial uses for these products to reduce waste and close materials loops and life cycles.

The National Energy Technology Laboratory has suggested that the continued use of coal in the nation's energy portfolio will require increased mitigation of the environmental impacts of coal burning and coal combustion by-products specifically (NETL, Trends). The increased demand for electricity and anticipated increases in coal generation and emissions controls will mean that coal combustion by-products in general, and spray dryer ash specifically, will continue to be available and in need of useful applications for the foreseeable future. However, legislation involving carbon cap and trade will have a significant impact on the coal and power industries in the near future. The continued combustion of coal by traditional methods may not be reliable and therefore the resulting ash supply may not remain consistent. Given industry built around CCBs and reduced ash availability, ash suppliers may be driven to reclaim stockpiled ash as coal combustion plants are decommissioned. With the quality and regional availability of CCBs currently in question and the future of ash supplies also uncertain, adaptive up-to-date research and rapid implementation of beneficial use applications will be paramount to decreasing environmental impact and improving the quality and durability of our built environment.

5.4.3 Economic Barriers

There is now wide recognition within academia and industry that fly ash is a critical component in high-performance Portland cement concrete and thus it has a certain market value. With further research, this may become the case with spray dryer ash as well. Robl and McCormick (2009) have identified three critical factors affecting the fly ash market that also apply to spray dryer ash: declining quality, value, and supply. They note that declining quality may result from new environmental controls increasing loss on ignition (LOI) or unburned carbon and sulfur content (i.e. in spray dryer ash). With respect to supply, fly ash is a compositionally varied and regional product dependent on processing conditions and the type of coal from which it is produced. Given the high cost of transporting a heavy, bulky, dust-prone material like fly ash, it has diminishing energy and resource returns the farther it is shipped. The quality and properties of a particular fly ash are only available cheaply near a particular coal combustion plant. Spray dryer ash has similar, if not wider, variability. The beneficial use of any ash may rely on local research and development efforts to effectively use a specific ash. Technology transfer between utilities, marketers, and private enterprises working with similar ashes is critical.

Other economic barriers may include limited demand, regional variability in quality and supply, industry inertia and unwillingness to try untested materials, the perception of unproven technology, competitive and political nature of ash marketing and utilization, high capital costs for new business startup including code-compliant shipping and handling infrastructure, and limited available research and case studies to convince decision makers.

Expanded discussions of the many barriers to implementation of CCBs in beneficial use applications are included in numerous discussions of the topic (e.g. EPRI, 2007 and EPA 2008).

5.5 Future Work

The potential for future use and therefore study of spray dryer absorber material is excellent. The barriers to implementation described above have associated research potential that can serve to break them down. Given the potential for beneficial use of SDA material and fly ash in general, the likely increases in production of these materials, and the relative lack of understanding of various aspects of the materials, their continued study is critical and many research topics exist.

Further testing is required to fully understand the behavior of the materials developed in this study. If the materials are to be used in structural applications, various properties need to be quantified in addition to the strength and stiffness properties tested here. These properties include splitting tensile strength, dry density, permeability, abrasion resistance (ASTM C 944), rebar pullout capacity, and bond strength (ASTM C 234). Freeze-thaw, sulfate resistance, and other long-term effects need to be investigated and environmental performance characteristics need to be further examined including leaching and off-gassing potential. Large-scale or full-scale testing of structural elements (e.g. testing by Cross et al., 2005) would be useful to investigate the impact of the reduced stiffness of the materials developed here.

Further development of the fiber-reinforced material would require testing for compliance with ASTM C 1116 – Standard Specification for Fiber-Reinforced Concrete. Some synthetic polymer fibers are known to degrade in the alkaline environment of a cement matrix. This potential would have to be investigated and guidelines are provided in ASTM C 1116.

The environmental conditions and material requirements for the various forms of sulfate attack require greater understanding in general. The specific contribution of the compounds inherent in spray dryer ash is critical to determining if this material can play a useful role in hardened structural and non-structural products. Any number of research tracks can be proposed here to examine sulfate attack in general and scientific terms or specifically with respect to hydrated spray dryer ash materials. With respect to the materials examined here, possible further testing could be conducted to determine the optimum SO_3 content for the mortars using ASTM C 563 – Standard Test Method for Approximation of Optimum SO_3 in Hydraulic Cement Using Compressive Strength. It would be interesting to see if this test shows that more or less SO_3 should be included in the mix. It would also be helpful to sample the Rawhide fly ash before it enters the spray dryer absorber process to more accurately describe the material and process. There could be benefits to changing the Rawhide system to include precollection of fly ash if the effectiveness of the fly ash in concrete were better prior to processing in the spray dryer absorber chamber.

A more detailed understanding of the material and its variability is critical to comprehending why the material behaves as it does. Thorough chemical and mineralogical analyses of the material and a statistical analysis of the variation in these properties based on the changing conditions at the coal combustion plant would be required for quality control and assurance. Chemical and mineralogical analysis of the material at various ages after hydration would also be very helpful in understanding the hydration process and its products in order to address concerns about ettringite and potential for thaumasite formation. Collaboration with cement chemists would improve the quality of the work and the explanations provided for observed changes in strength and other properties. The exact strengthening mechanism resulting from the addition of Portland cement is merely conjecture and needs to be investigated more completely. Additional parametric studies with added activation materials like lime and alkali compounds or mechanical methods like ball milling could be useful in producing a stronger hardened product or more reactive ash.

Glossary

ACI – American Concrete Institute

ASTM – American Society for Testing and Materials (now ASTM International)

CCB – coal combustion by-product

CCP – coal combustion product

CLSM – controlled low-strength material

Dry FGD material – any dry material resulting from flue gas desulferization including spray dryer absorber material

FBC – Fluidized Bed Combustion (a process of coal combustion)

FGD – Flue Gas Desulferization

HVFA concrete – high-volume fly ash concrete

PCC – Portland cement concrete

PRPA – Platte River Power Authority

RMC – Recovered Mineral Component

RPS – Rawhide Power Station

SDA – Spray dry absorber, the chamber where flue gas desulferization occurs

SDA material – spray dry absorber material (also called spray dryer ash)

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Appendix A

Compressive Strengths Plotted with Sample Variation

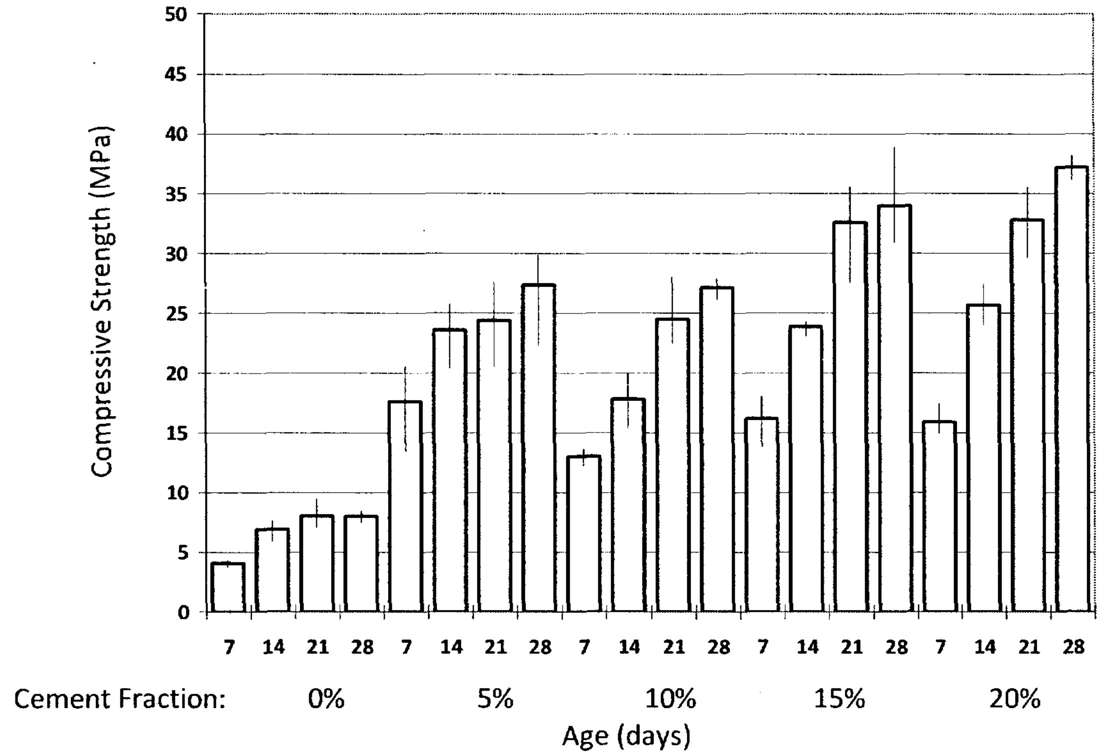

Figure A1. Compressive strength versus age for varied Type I/II cement fraction and zero fiber fraction.

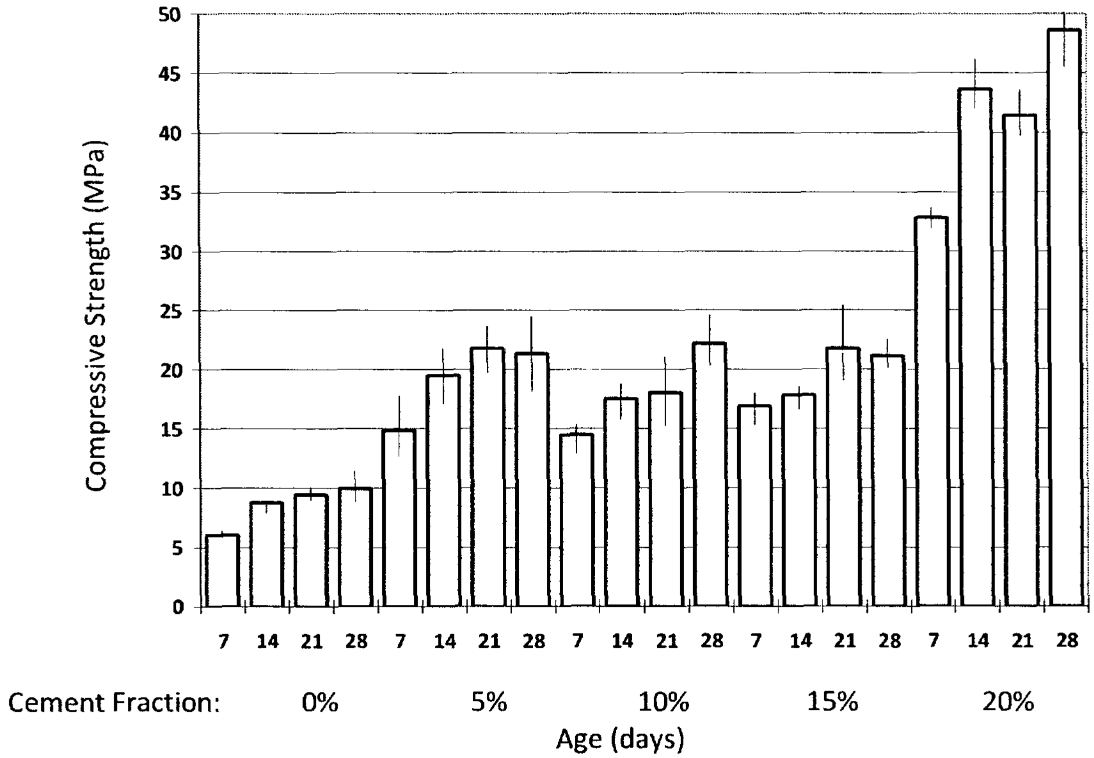

Figure A2. Compressive strength versus age for varied Type I/II cement fraction and 0.5% fiber fraction.

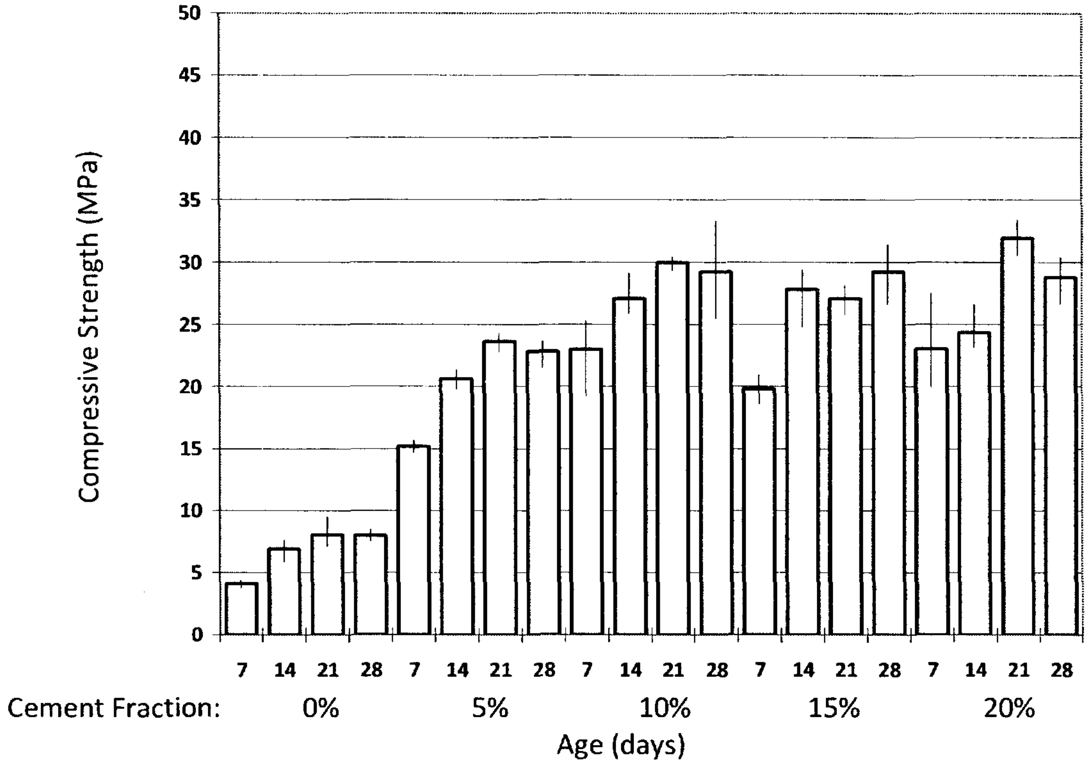

Figure A3. Compressive strength versus age for varied Type III cement fraction and zero fiber fraction.

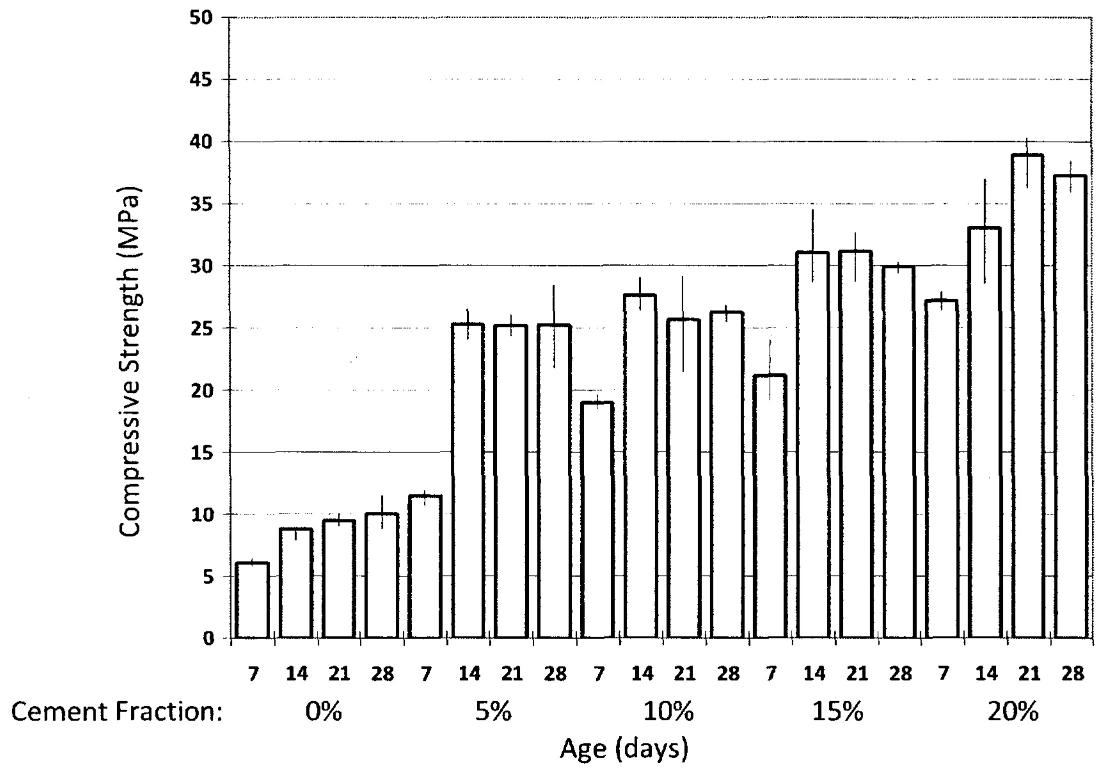

Figure A4. Compressive strength versus age for varied Type III cement fraction and 0.5% fiber fraction.

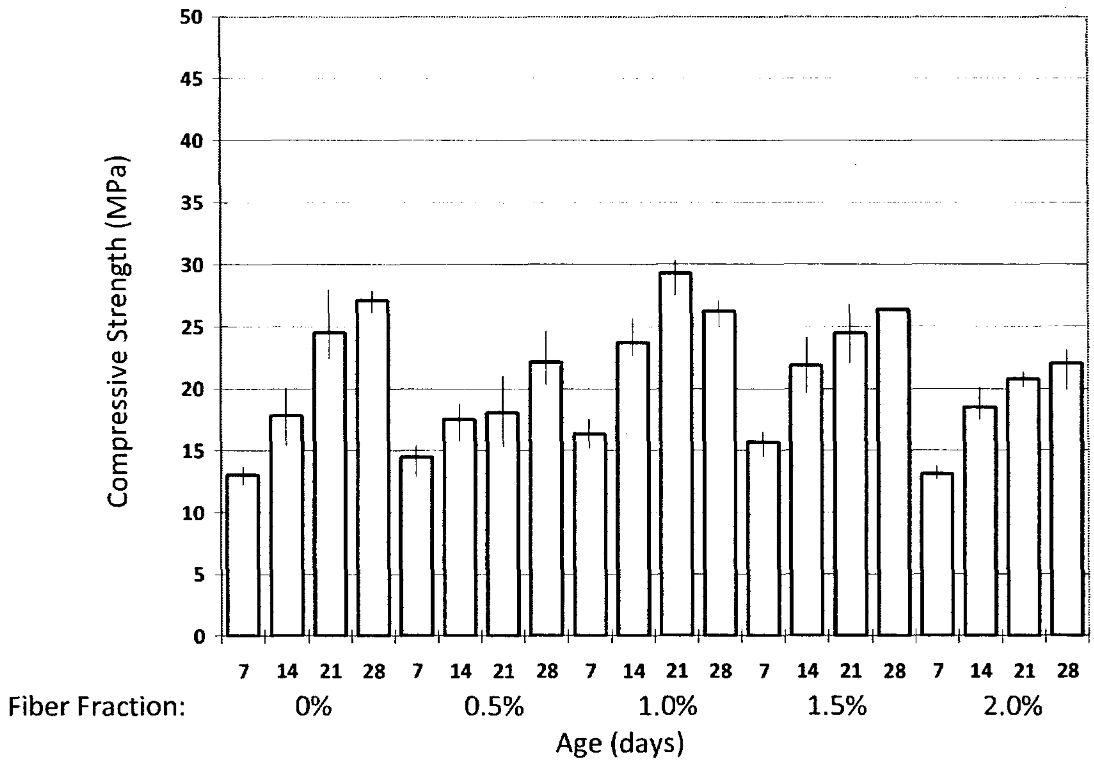

Figure A5. Compressive strength versus age for 10% Type I/II cement fraction and varied fiber fraction.

Appendix B

Compressive Modulus of Elasticity Plotted with Sample Variation

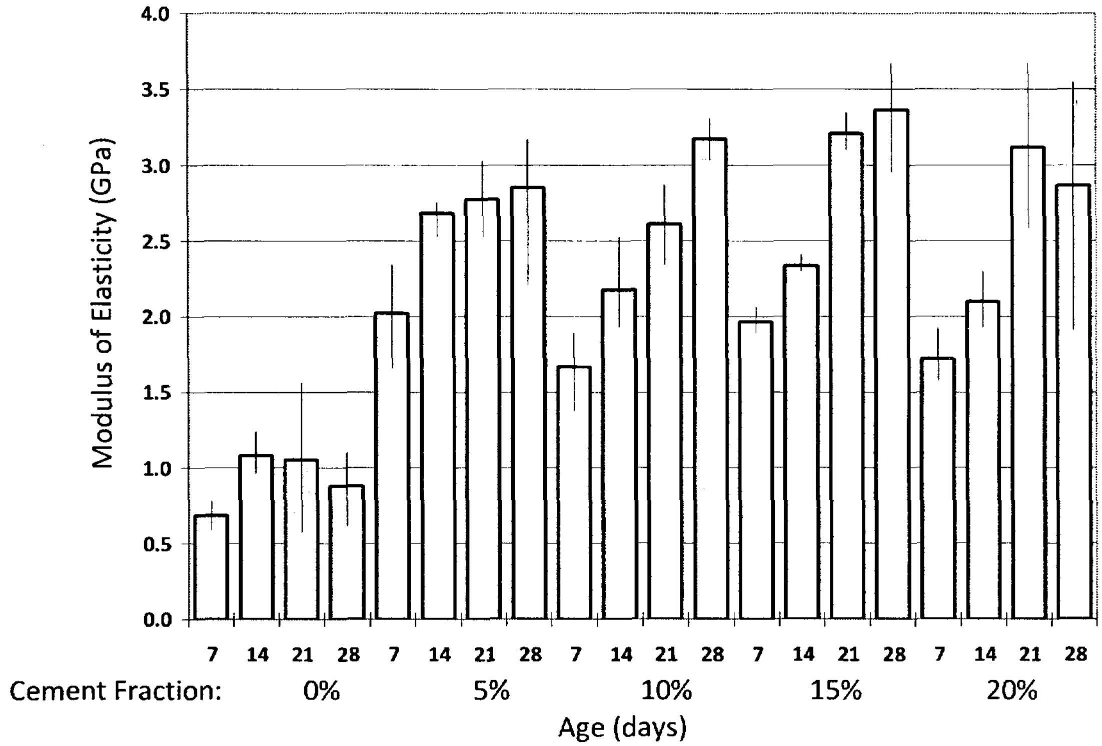

Figure B1. Modulus of elasticity versus age for varied Type I/II cement fraction and zero fiber fraction.

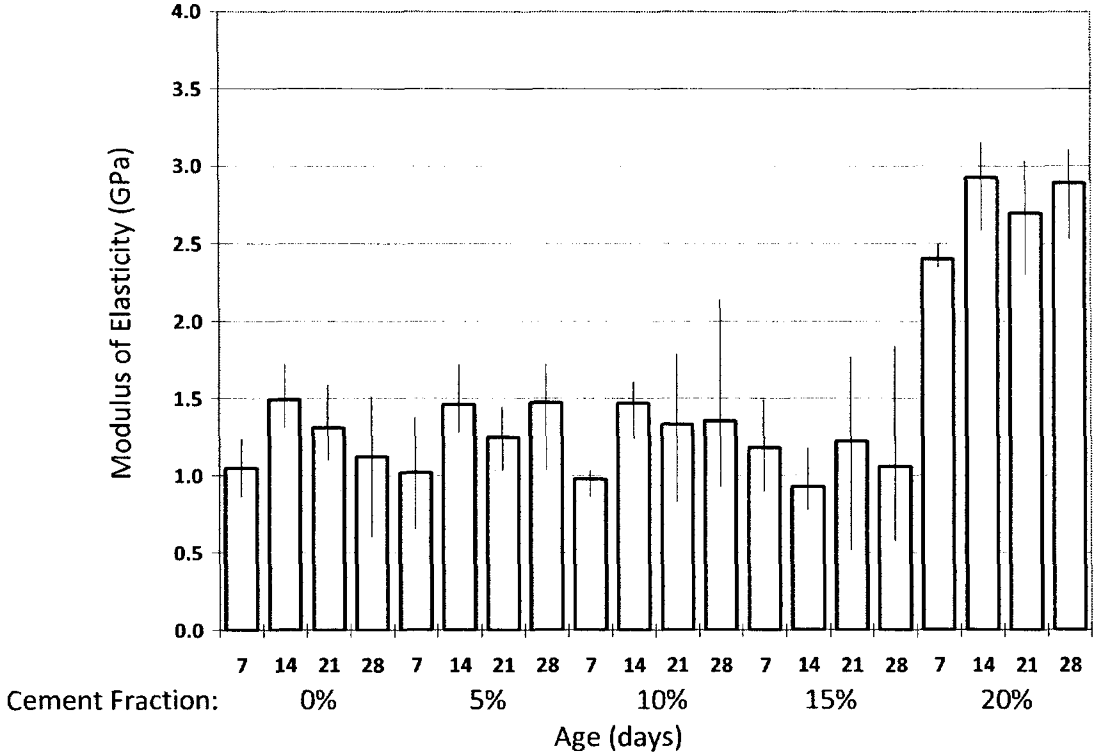

Figure B2. Modulus of elasticity versus age for varied Type I/II cement fraction and 0.5% fiber fraction.

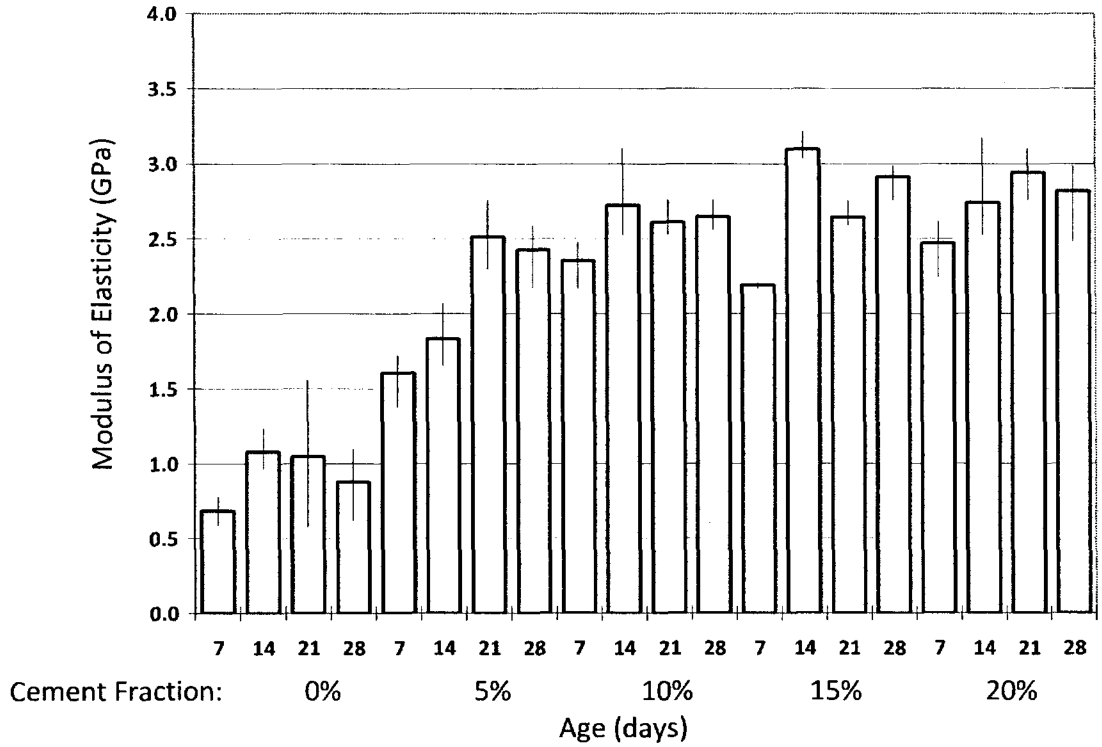

Figure B3. Modulus of elasticity versus age for varied Type III cement fraction and zero fiber fraction.

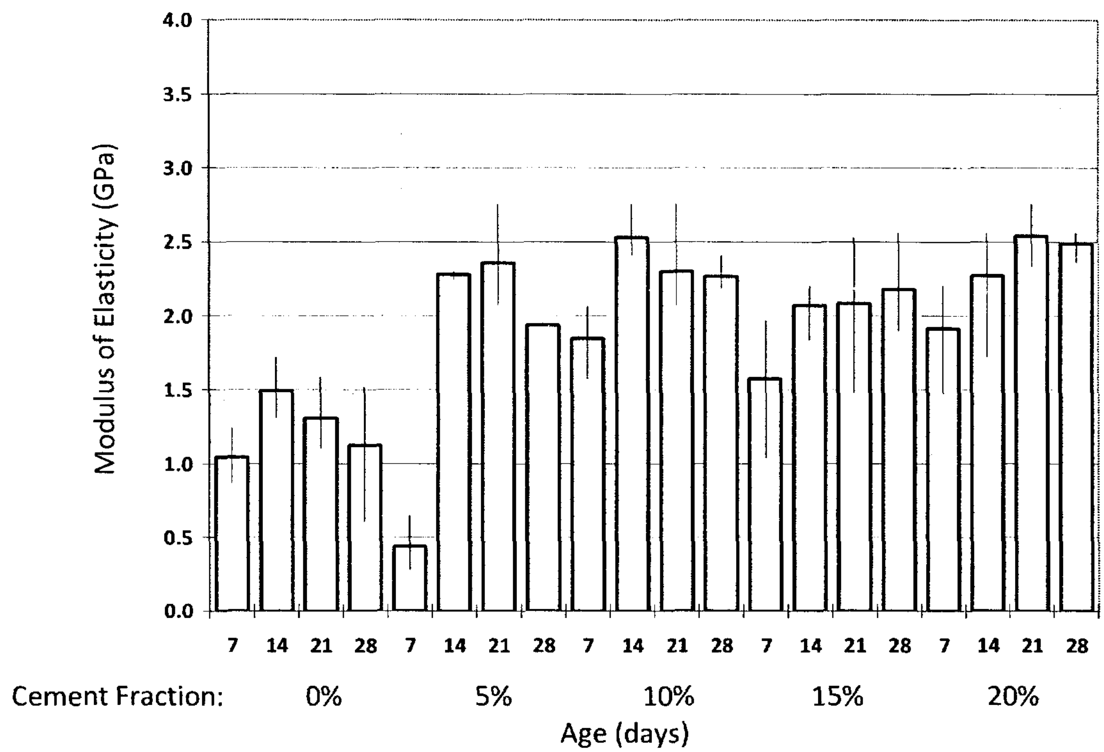

Figure B4. Modulus of elasticity versus age for varied Type III cement fraction and 0.5% fiber fraction.

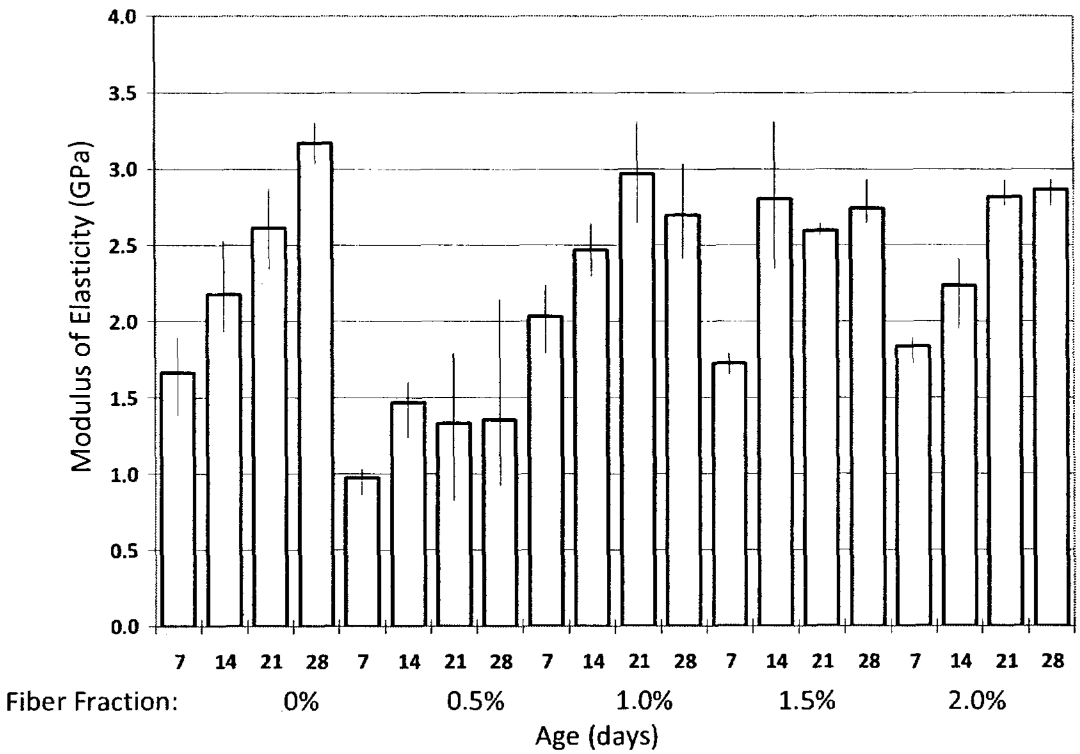

Figure B5. Modulus of elasticity versus age for 10% Type I/II cement fraction and varied fiber fraction.

Appendix C

Modulus of Rupture Plotted with Sample Variation

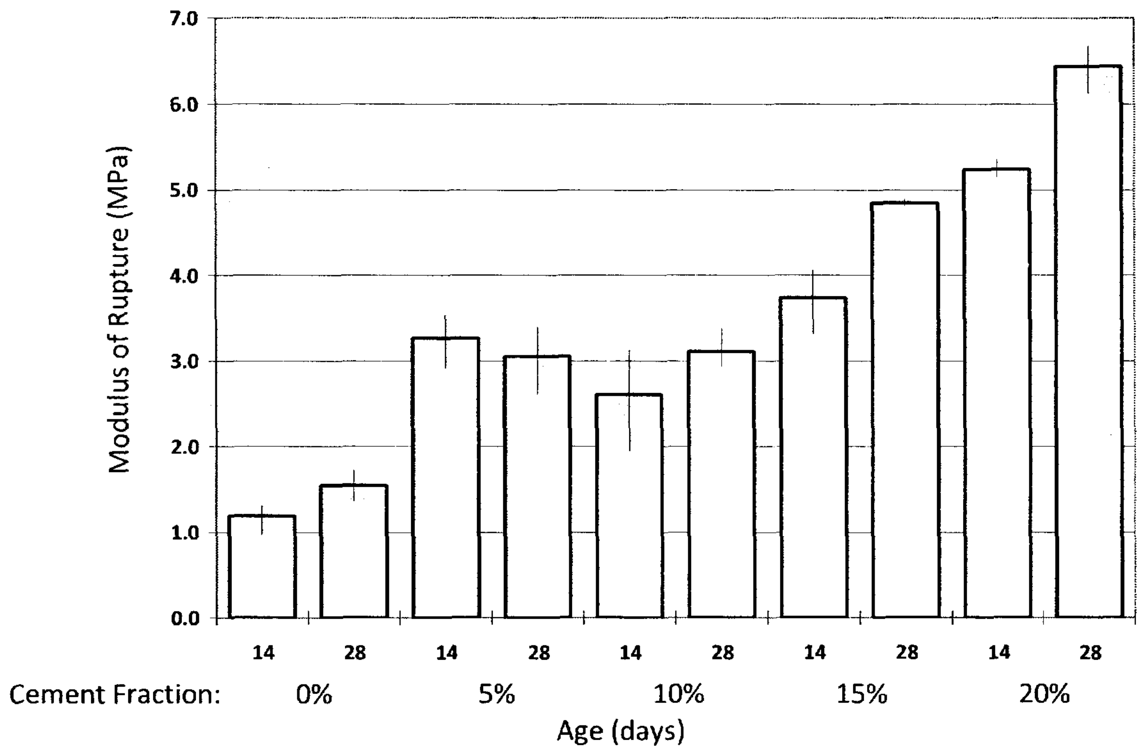

Figure C1. Modulus of rupture versus age for varied Type I/II cement fraction and zero fiber fraction.

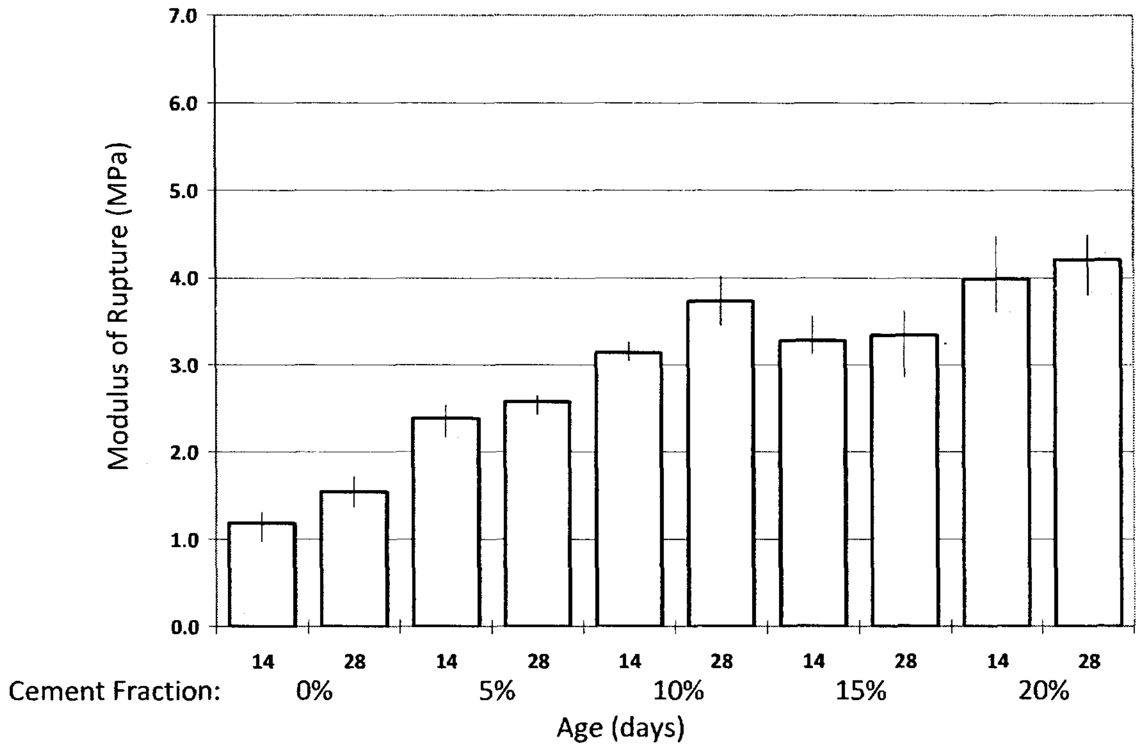

Figure C2. Modulus of rupture versus age for varied Type III cement fraction and zero fiber fraction.

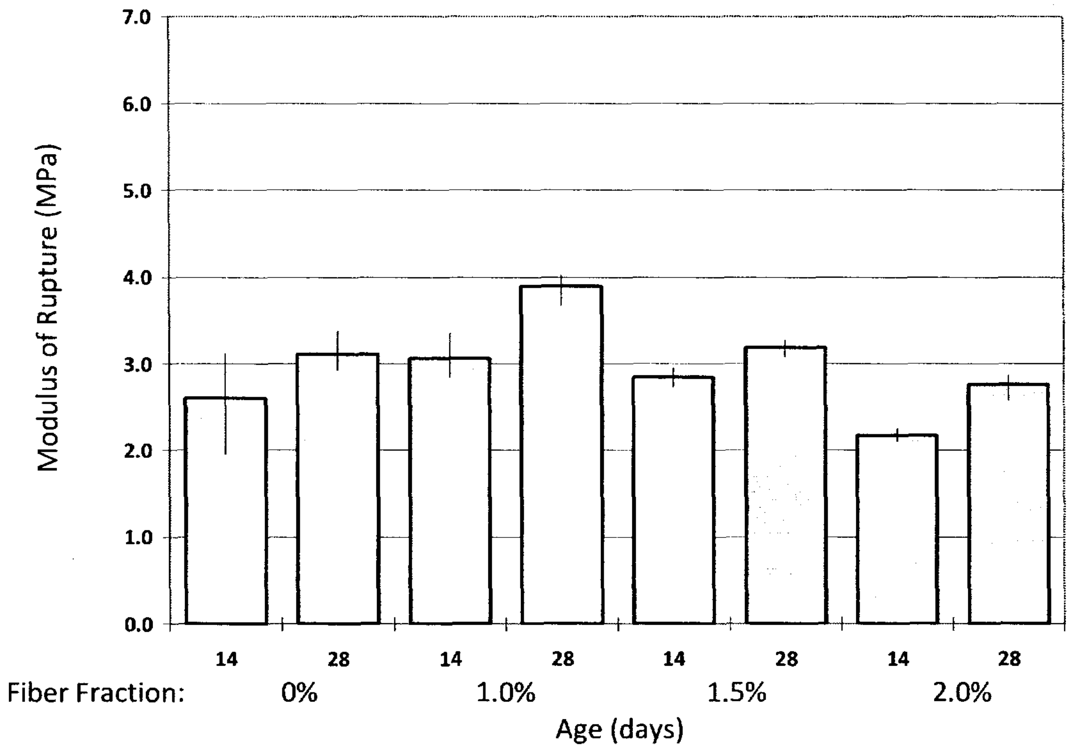

Figure C3. Modulus of rupture versus age for 10% Type I/II cement fraction and varied fiber fraction.