Identification and Verification of Self-Cementing Fly Ash Binders for "Green" Concrete

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ABSTRACT

Researchers at Montana State University are engaged in an effort to identify fly ashes (a byproduct of coal fired power plants) from around the country that are capable of replacing 100 percent of the Portland cement as the binder in conventional concrete. These ashes are further being used in concretes in which recycled/pulverized glass is being used as the aggregate to produce a "green" concrete. Work on this effort began with a review of the major macro-scale factors known to affect the self-cementitious properties of fly ashes (i.e., coal type, combustion process, and emission controls). Based on these macro-scale criteria a large database of 491 power plants was screened and 15 ashes were identified for further consideration. Concrete mixes were made with samples of these 15 ashes (consisting of fly ash, recycled glass, water, and a set retarding admixtures), and selected engineering properties were evaluated. Of these 15 fly ashes, 8 produced concretes with 28-day compression strengths of at least 20.68 MPa (3,000 psi), making these concretes potentially viable for standard construction applications.

INTRODUCTION

Approximately 7 billion cubic yards of concrete are produced per year, making it the second most consumed substance on earth (next to water). Unfortunately, conventional concrete production emits large volumes of greenhouse gasses and greatly disrupts virgin lands. Using "green" materials in concrete instead of Portland cement and natural aggregates will help mitigate concrete's adverse effect on the environment. Additionally, if common waste-streams are used as replacements, the environmental advantage is twofold, that is, issues associated with using virgin materials are voided and the volume of two significant waste-streams is reduced.

The production of Portland cement is an energy intensive process which requires heating of raw materials to temperatures in excess of 2500°F. In this process, CO_2 is emitted from both fuel combustion and decarbonation of limestone, with more CO_2 actually being produced than cement (by weight). Thus, due to its widespread use, Portland cement is responsible for 7 percent of the worldwide greenhouse gas emissions (according to data from 2004).[1] In addition, cement production and the resulting emissions are expected to double from the current level by the year 2020.[1]

Fly ash (a byproduct of burning coal to produce electricity) can have cementitious behavior similar to that of Portland cement. The type of coal burned and the nature of the combustion process at the power plant have a major effect on the binding properties of the resulting ash. Since power plants use a variety of coal types and burning processes, the behavior of ash can vary considerably from plant to plant; as a result, fly ash is typically used to replace no more than 25 percent of the Portland cement in concrete. By gaining a deeper understanding of the behavior of different fly ashes, their binding capacities can be more advantageously used. Increasing the use of fly ash will not only reduce the greenhouse footprint of concrete, but also provide a constructive use for the 39 million tons of fly ash which are unused each year in the United States (according to data from 2004).[2] Realizing these environmental advantages, there is ongoing research to develop high volume fly ash concretes, although generally these concretes still incorporate a significant amount of Portland cement.

Aggregates typically account for 70 to 85 percent, by weight, of the material used in concrete. Due to the large volume of concrete produced, the attendant mining of natural aggregate for concrete greatly disrupts virgin land. Using recycled material as aggregate not only lessens the demand for mined aggregate, but also decreases the demand on landfills. Pulverized post-consumer glass is one such recycled material that merits consideration as concrete aggregate. Americans generated 13.2 million tons of glass in 2006, of which only 22 percent was recovered for reuse.[3] To create new containers from recycled glass, the old glass must be separated by color, which is difficult and expensive. In addition, it may be uneconomical to transport recycled glass to the container manufacturer. Therefore, in some instances, glass that is collected with the intent of recycling is crushed and thrown away due to a lack of economical alternatives. Using glass as concrete aggregate offers a new environmentally friendly means by which recycled glass could be consumed.

An environmentally friendly concrete can be made through using recycled pulverized glass as the aggregate and fly ash as the sole binder. While such a concrete is appealing in theory, is it feasible in reality? This question was partially answered in 2008, when Montana State University/Western Transportation Institute (MSU/WTI) performed the research for the first major commercial project constructed using 100 percent fly ash concrete with glass aggregate, namely, a branch of the Missoula Federal Credit Union in Missoula, MT.[4]The fly ash for the project was from the Corette Power Plant in Billings, MT, and the MT Department of Environmental Quality provided the glass. Fly ash and glass concrete was used to construct both structural and nonstructural elements in the building. While the project was a success, research is needed to further investigate the fundamental engineering properties, durability, and the applicability of existing design procedures for this new material. Furthermore, while research with the Corette ash has set the stage for a 100 percent “green” concrete, identifying suitable fly ashes throughout the country for use in fly ash based concrete is essential to fully realize the benefits this material offers. This is the primary objective of the research to be discussed herein.

This study focuses on identifying potential sources (i.e., power plants) for fly ash capable of serving as the sole binder in fly ash and glass concrete. This screening was accomplished using criteria related to coal type, combustion process, and emission controls, all of which are known to affect the self-cementing properties of fly ash. These criteria were applied across an inventory maintained by the U.S. Energy Information Association (EIA) of 491 coal-fired power plants. Based on this review, 96 potential sources of fly ash were identified. Suppliers of these fly ashes were contacted to obtain additional information on, and samples of these ashes. Samples of 15 ashes were subsequently received from power plants around the country. These samples were used to produce several bench-top concrete mixes, which were used to evaluate the potential suitability of each fly ash as the sole binder in fly ash and glass concrete. The properties of particular interest in these mixes were set time, workability, strength (reported on herein), and hydration-temperature behavior (as an indicator of set time and the relative nature of the cementitious reactions that occurred). The results of these tests were used to check the efficacy of the initial ash selection criteria, as well as to search for other readily available ash properties that correlate well with subsequent engineering performance.

FLY ASH EVOLUTION

Fly ash is a by-product of the combustion of coal to generate electricity. After the coal is delivered to the power plant, it is pulverized and ignited in a furnace/boiler. The high temperature in the boiler burns off the volatile matter and carbon, leaving behind mineral impurities from the coal in the form of a molten ash. The ash particles fuse together in the combustion zone and condense upon leaving this zone, forming glassy particles. The fine light particles exit the furnace at the top with the combustion gases and are termed fly ash, while the course/heavy particles fall to the floor of the furnace and are termed bottom ash. Fly ash is removed from the flue gasses and collected in an effort to reduce the adverse effects of coal-fired plants. Additional emission controls are often used to reduce the amount of sulfur dioxide, nitrogen oxide, and mercury released to the atmosphere. While the minerals present in the coal mainly influence the chemical constituents of fly ash, the mineralogy and crystallinity of fly ash produced from the same coal source can vary significantly depending on the coal combustion technology used. Since the coal sources and the devices used to burn and collect the ash and control emissions vary from plant to plant, the reactivity and characteristics of fly ash varies between electricity generating stations.

Coal and Fly Ash

Currently, the electric power sector accounts for 90 percent of the of the coal consumed in the United States.[5]The nation's large coalfields satisfy the high domestic demand for coal. There are 458,000 square miles of underlying coal deposits in the United States, which is approximately 13 percent of the total land area.[6] In 2008 alone, 1,171.8 million short tons of coal were mined in the United States.[7] The majority of this coal (almost 90 percent) comes from five regions, the Appalachian Region, the Powder River Basin, the Illinois Basin, the Gulf Coast Region, and the Fort Union Region. The greater part of the remaining coal (about 8 percent) is produced in the southwestern United States in the Unta Region, the Raton Mesa Region, the Green River Region, the Black Mesa Region, and the San Juan Basin.[8] Coal from each region is ranked on its carbon content and therefore its ability to produce heat. The four ranks of coal (from most to least carbon content) are: anthracite, bituminous coal, subbituminous coal, and lignite. Because of its similarity to bituminous coal, anthracite is often categorized as bituminous coal, as is done in the U.S. Energy Information Administration (EIA) databases (to be discussed later). The behavior and classification of fly ash is directly related to the rank of the coal from which it is produced.

According to ASTM C618, Class F fly ash is normally produced from burning anthracite or bituminous coal and has pozzolanic properties.[9] Conversely, Class C fly ash is typically produced from burning lignite or subbituminous coal, and in addition to having pozzolanic properties, has some self-cementitious properties. As previously mentioned, the chemical constituents of fly ash mainly depend on the chemical composition of the coal source. Generally, anthracite and bituminous coals contain less calcium oxide (CaO) than lignite and subbituminous coals. As a result, the CaO content of Class C fly ash (usually 10 to 40 percent) is higher than the CaO content of Class F fly ash (typically less than 10 percent).[10] The high calcium content of Class C fly ash allows it to be more reactive with water than a traditional pozzolan.

Pozzolanic materials are typically high in SiO_2 and Al_2O_3, and low in CaO; therefore, they have little or no reactivity when immersed in water. However, in the presence of water and $Ca(OH)_2$, pozzolans will chemically react to form compounds possessing cementitious properties.[9] The basic pozzolanic reactions are:

- $Ca(OH)_2 \rightarrow Ca^{++} + 2[OH]^-$,
- $Ca^{++} + 2[OH]^- + SiO2 \rightarrow CSH$, and
- $Ca^{++} + 2[OH]^- + Al_2O_3 \rightarrow CAH$.

The calcium content in Class C fly ash allows the reactions above to occur without the addition of calcium from an external source. In class C fly ash-water pastes, calcium aluminosilicate hydrate (CAH) minerals such as strätlingite, ettringite, and monosulfoaluminate can be identified, while the formation of calcium silicate hydrate (CSH) is difficult to measure with laboratory equipment.[11] The CSH, however, probably accounts for a significant portion of the observed strength gain in fly ash pastes made from high calcium fly ash.[8]

Coal Combustion Process

When coal is fired in a furnace the high temperatures (about 2700°F) melt or partially melt the mineral matter in the coal leaving behind glassy fused particles. Fly ash is primarily made up of glass (75 to 90 percent), which dissolves in high pH solutions, and has a highly variable structure. Glass composition depends on the modification by ions in the glass (such as Ca, Na, K, Mg, and Fe) and on the rate of quenching.[12] These ions act as network modifiers, reducing the long-range order of the glass, which causes an increase in the rate at which it can be dissolved.[8] In addition to glass, crystalline minerals are formed during the combustion of coal. When molten elements react with oxygen, crystalline minerals form either on the surface of the fly ash glass or embedded inside the glass particles, depending on the temperature and furnace conditions. Some of these crystalline compounds react with water, which increases the pH and allows the glass to dissolve and cementitious bonds to form. The self-cementitious behavior of fly ash is highly subject to the heating and cooling conditions experienced within a boiler.

Dry bottom, pulverized fuel boilers and wet bottom (slag tap) boilers are the two traditional combustion systems mainly used for electricity production. The main difference between the two boiler types is the temperature at which they operate. In dry bottom boilers, the flame temperature is below the ash melting point and there is sufficient cooling to enable the particles, which are partly melted in the flame, to solidify. As a result, both the bottom ash and the fly ash leave the furnace in a dry state. Since wet bottom boilers have two chambers (the combustion chamber and the heat exchange chamber), they operate at higher temperatures than dry bottom boilers. The combustion chamber is barely cooled and temperatures exceed the ash melting point, which causes molten ash to flow to the bottom in a molten state. The ash that does not agglomerate in the combustion chamber passes into the heat exchange chamber where it is cooled along with the flue gases. In general, only 40 to 50 percent of the ash from a wet bottom boiler is fly ash, while 80 to 90 percent of the ash from a dry bottom boiler is fly ash.[13] Additionally, the fly ash from wet bottom boilers is sometimes recirculated to the furnace where it is reheated and agglomerates to become bottom ash. Hence, some wet bottom boilers produce essentially no fly ash as a byproduct.

The temperatures inside a boiler are governed by both the burner type and burner placement within the boiler. Two main types of burners are used in dry bottom boilers, namely: swirl burners and jet burners. There are three main options for the placement of the burners. These options, are wall front-fired, wall opposed-fired, and corner tangential-fired (Figure 1). In a boiler, fuel and air must be mixed to allow the coal to burn efficiently (this allows elements to react with oxygen, forming crystalline minerals). Swirl burners mix the air and fuel at the burner itself and are often used in wall front-fired and wall opposed-fired boilers. Since jet burners have no mixing of air and fuel at the burner, they are used in corner tangential-fired systems. The tangential placement of the burners creates a rotating flame or fireball located in the center of the furnace.

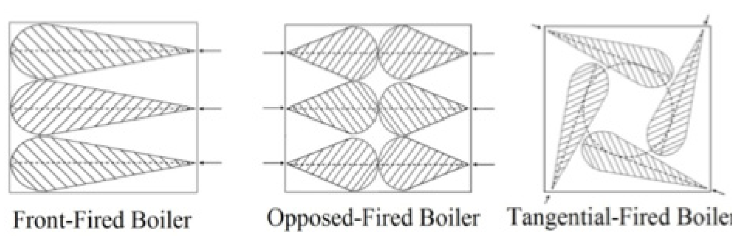

Figure 1: Options for Burner Placement[13]

The circulating flue gases from this flame cause the fuel and air injected into the furnace to mix. In general, tangential-fired boilers have one large flame inside the furnace while wall front-fired and wall opposed-fired boilers have small discrete flames located at each burner. As a result, tangential-fired boilers have lower peak burner temperatures than front-fired and wall opposed-fired boilers. Due to the temperature difference, it is expected that the firing arrangement has some affect on the cementitious behavior of fly ash, but the extent of this affect is unknown.

In an effort to reduce emissions, advanced combustion technologies have been recently developed which integrate emission controls within the combustion system. The three main advanced combustion systems identified by EIA are: atmospheric fluidized bed combustion, pressurized fluidized bed combustion, and integrated gasification combined cycle.[13] As expected, these combustion technologies have a varying affect on fly ash. In one study, fly ash from a fluidized bed combustion boiler was especially different from coal ash from traditional pulverized fuel firing due to many differences in their combustion processes.[14] While advanced combustion technologies may have a more predominate effect on fly ash in the future, converting boilers to the fluidized-bed combustion process and employing the technology of integrated gasification combined cycle are currently under study and are not in extensive use according to the EIA.[15]

In addition to using advanced combustion technologies, some electrical generation stations have turned to biomass co-firing to reduce emissions (especially greenhouse gas emissions). “Biomass” includes any natural, renewable fuel, such as agricultural residues, wood/wood waste, food wastes, and industrial wastes. Burning additional types of fuel in the furnace/boiler with the coal will most likely have an effect on the fly ash. The utilization of co-combustion residues can be restricted by the unburnt carbon content when high percentages of biomass flues are mixed with coal.[16] In addition to biomass, some power plants burn secondary fuels with the coal (such as waste coal, petroleum coke, natural gas, fuel oil, etc) for various reasons, which can have an effect on the use of the fly ash.

Emission Controls

Two types of emissions are produced as a result of generating electricity at a coal fired power plant: gaseous and particulate. Particulate control devices remove fly ash from the flu gas while gaseous control devises are used to hinder the release of sulfur dioxide (SO_2), nitrogen oxides (NO_x), and mercury to the atmosphere. Over the years, numerous methods of targeting and reducing the release of particulate and gaseous emissions have been developed. Pollution control technologies have a varying impact on the usability of fly ash in green concrete.

Particulate Controls

Fly ash is removed from the flue gas using a wet particulate scrubber, an electrostatic participator (ESP), or a baghouse. Wet particulate scrubbers capture fly ash particles in the scrubber slurry droplets. A dewatering system allows the ash to be removed from the slurry and collected. ESPs remove fly ash using an electrostatic charge that attracts fly ash particles to metal collection plates. A rapping system is used to knock the ash from the plates, allowing it to fall into a hopper below. Baghouses collect ash on a fabric filter as the flue gas passes through the fabric. Periodic shaking of the bags, reverse flue gas flow, or compressed air pulses removes the ash from the filter where it falls to the hopper below.

According to the Electric Power Research Institute (EPRI), fly ash which is collected or handled wet generally cannot be used in high-value applications such as cement replacement.[17] Fly ash loses its self-cementing ability after it is exposed to water and hydration reactions occur. As a result, fly ash captured using wet particulate scrubbers cannot be used in 100 percent fly ash concrete. In addition, some fly ash is collected dry and transported by a wet sluice system. This ash is also generally unsuitable for use in fly ash concrete.

The ability for an ESP to effectively remove fly ash from the flue gas is highly dependent on the resistivity (ability to accept an electrical charge) of the ash. If an ash's resistivity is too high, the particles do not migrate to the collecting plates. Conversely, if an ash's resistivity is too low, the particles clamp to the plates and are difficult to remove. These issues are resolved using two methods: fly ash resistivity conditioning and fly ash cohesivity conditioning. Injecting SO_3 or evaporating water in the flue gas is effective in resistivity conditioning of the fly ash, allowing the particles to accept a charge. Resistivity conditioned systems typically have only minor impacts on the fly ash, increasing the ash sulfate and/or moisture content by small percentages.[17] Injecting ammonia into the flue gas is effective in cohesivity conditioning of the fly ash. The addition of ammonia helps alter the fly ash surface charge which enhances particle agglomeration, allowing the ash to fall from the collecting plates.[18] As a result of flue gas conditioning, ammonia concentrations up to about 250 ppm have been observed in fly ash.[19] The sharp, irritating, pungent odor of ammonia vapor released when fly ash with high ammonia concentrations is hydrated can make the ash unusable even though ammonia in fly ash has been shown to have little effect on the physical-chemical-mineralogical properties of the ash.[20]

Baghouses are excellent in controlling particulate matter emissions from coal-fired power plants. Well-operated baghouses can maintain outlet emissions well below regulatory standards with some units attaining fly ash collection efficiencies of over 99.9 percent.[21] Unlike other particulate collection methods, baghouses do not require fly ash conditioning, nor do they expose the fly ash to water. As a result, baghouses themselves do not negatively impact the use of fly ash for green concrete.

Mercury Emission Controls

In 2000, the EPA decided that mercury emissions from coal-fired power plants should be regulated. The agency has yet to set a maximum achievable control technology (MACT) standard, as required by the Clean Air Act.[22] Several bills have been introduced to Congress addressing mercury emission from power plants. Some bills have specified time frames for EPA to promulgate a MACT regulation and specific limits on mercury emissions from power plants. As a result of the current political movement in this area, it is expected that the volume of fly ash affected by mercury emission controls will increase significantly in the near future.

Mercury is not readily collected in fly ash since fly ash is composed predominantly of non-combustible minerals that have little capacity to absorb mercury. Introducing a carbon source to the system is one approach for absorbing the mercury, allowing it to be collected with the fly ash. Carbon is typically added to the system by modifying the boiler combustion to add unburned carbon, or by injecting activated carbon into the flue gas duct upstream of the particulate collection devices. Both of these methods not only increase the mercury content of the fly ash, but the carbon content as well. Studies by EPA, EPRI, and EERC have shown that mercury is not readily released from fly ash.[17] An increase in the carbon content can negatively affect the air-entraining properties of concrete made with the fly ash. Entrained air in concrete is required for adequate freeze/thaw resilience. In an effort to reduce the impact of activated carbon injection on fly ash, some power plants have implemented proprietary processes that inject activated carbon downstream of the particulate control device. A compact fabric filter then collects the mercury, carbon, and a small percentage of the fly ash. As a result, the majority of the fly ash has no elevated carbon or mercury content. As foretold, carbon-based mercury sorbents can negatively affect the reuse of fly ash. Consequently, a number of mineral-based sorbents are being developed to avoid impacts on fly ash, but these sorbents are not yet widely used.

NO_x Emission Controls

Four primary technology types are used to control NO_x emissions, namely: furnace combustion modifications, selective non-catalytic reduction (SNCR), selective catalytic reduction (SCR), and rich reagent injection (RRI). All four of these technologies are introduced into the system upstream of the particulate collector and therefore can adversely impact the fly ash.

Combustion modifications (including the use of low-NO_x burners) limit the availability of oxygen during the coal combustion process, which in turn controls the formation of NO_x. Limiting the available oxygen during combustion makes it difficult to achieve complete fuel combustion, which can result in an increased loss on ignition (unburned carbon) in the fly ash.

SNCR and SCR are both used to chemically reduce the NO_x formed in the furnace through the use of oxidation/reduction reactions between ammonia and NO_x. The only difference between SNCR and SCR is that SCR technology uses a catalyst to provide active surface area on which the oxidation/reduction reactions can take place. This causes SCR systems to have much lower ammonia slip (i.e. the release of unreacted ammonia) than SNCR systems, resulting in fly ash with lower ammonia content.

Urea or ammonia is injected into fuel-rich portions of the furnace to decrease the formation of NO_x in RRI systems. RRI technology can be used in conjunction with low-NO_x burners and/or SNCR systems. Typically, the majority of the urea or ammonia injected into the furnace is destroyed within the boiler, causing ammonia slip to be fundamentally nonexistent. Accordingly, the fly ash ammonia contamination is minimal or nonexistent if RRI alone is implemented on a unit.[17]

SO_2 Emission Controls

Flue gas desulfurization (FGD) is a technology used to remove SO_2 from the flue gas. FGD systems can be generally categorized as “wet” or “dry.” The majority of wet FGDs are preceded by the particulate control device and therefore have no affect on the fly ash. Dry FGD systems come in two forms: spray drying and dry injection.

Spray drying FGD systems introduce a finely atomized slaked-lime-based aqueous slurry to the flue gas. The spray dryer is typically located upstream of the particulate collector, mixing the spray-dried product with the fly ash. Typically, over a quarter of the solids collected using a spray dryer FGD system is not fly ash. Thus, the dry product is commonly land filled.

Dry injection of sodium alkali, into the system is sometimes used to reduce SO_2 emissions. As a result, the fly ash contains a mixture of sodium sulfate and excess sodium alkali. The injection of limestone or hydrated lime is also used to reduce SO_2 emissions. This technology in general adds a considerable amount of calcium sulfate, calcium carbonate, lime, and/or hydrated lime to the fly ash. This additional calcium content could potentially increase the self-cementitious behavior the fly ash.

FLY ASH SELECTION PROCESS

According to the U.S. Government Accountability Office, there are 491 coal-fired power plants in the United States.[22] It was expected that a portion of these power plants produce fly ash that is suitable to use in 100 percent fly ash concrete, similar to the fly ash successfully used to-date in this application from the Corette power plant. The Corette power plant burns a subbituminous (Powder River Basin) coal in a tangentially fired dry bottom boiler with ESP particulate control. Since this project began, the plant instituted an unburned carbon mercury emission control system (the effect of this system on ash performance in concrete is only now being evaluated).

To determine which power plants were expected to produce useable fly ash, a selection criterion was developed to eliminate power plants based on coal sources, coal combustion processes, and emission control technologies which are known to adversely affect the self cementing ability of fly ash (as discussed in the previous section). Several databases on coal-fired power plants were obtained from the EIA, to which the selection criterion was applied.

The EIA is a statistical and analytical agency within the U.S. Department of Energy, and it conducts a comprehensive data collection program that covers the full spectrum of energy sources, end uses, and energy flows.[15] Two main forms that are used to collect information from power plants are the EIA-860 and the EIA-923.

Form EIA-860, “Annual Electric Generator Report,” contains information from power plants that is generator-specific such as generating capacity, energy sources, and generators ability to use multiple fuels. Schedule 6 of the EIA-860 form has detailed information related to the boiler(s) used at the power plant, including boiler air emission standards, design parameters and emission controls, cooling system design parameters, flue gas particulate collector information, flue gas desulfurization (FGD) unit design parameters, and stack and flue design parameters.

The Form EIA-923, “Power Plant Operations Report,” is used to collect monthly data on electric power generation and fuel consumption, stocks, receipts, quality, costs, fuel supplier, and coal mine source from utility and nonutility power plants. Monthly data is collected from a sample of power plants throughout the United States. Annual data is collected from the remaining plants that are not included in the monthly sample.

Coal Type

Since Class F fly ash has minimal self-cementitious properties, it was desired to eliminate power plants that produce this class of fly ash. However, the EIA-860 and EIA-923 databases do not provide information on fly ash class, but they do provide the rank of the coal that is burned at each plant. All power plants that burn anthracite and bituminous coal were eliminated since these coal sources generally produce Class F fly ash. Of all coal burned by power plants in the United States in 2004, DOE estimates that about 46 percent was bituminous (including anthracite), 46 percent was subbituminous, and 8 percent was lignite.[22] Even though the combustion of lignite typically leads to the creation of Class C fly ash, sources burning lignite were eliminated due to its small percentage of use compared with subbituminous coal. Thus, only power plants that burned subbituminous coal were further reviewed (150 plants).

Coal Combustion

The EIA-860 database provides a large quantity of data on the coal combustion process at power plants. This information includes: secondary fuel sources (coal, natural gas, biomass, etc), boiler type (wet or dry bottom), and firing type (e.g., front, opposed, tangential, fluidized bed).

The fly ash sources to be considered were further reduced to 128 in number based on secondary fuel sources, which were expected to have a negative effect on the fly ash. The EIA-860 database showed that numerous power plants burning subbituminous coal burn bituminous coal as a secondary fuel source. The self-cementitious behavior of an ash from such a plant could be greatly compromised depending on the ratio of bituminous versus subbituminous coal burned. Additionally, some power plants were shown to burn biomass, waste coal, wood waste, etc., which could potentially hinder the fly ash's performance as a binder. As a result, only ashes with no secondary fuel source or relatively clean burning secondary fuel sources (such as propane, natural gas, distillate fuel oil, etc) were considered for further investigation.

As mentioned previously, the self-cementitious behavior of fly ash is dependent on the temperature conditions within a boiler. Since wet bottom boilers operate at higher temperatures than dry bottom boilers (above the ash melting point versus below) and because the Corette power plant uses a dry bottom boiler, the power plants using wet bottom boilers were eliminated. Note that wet bottom boilers typically produce a significantly smaller fly ash to bottom ash ratio than dry bottom boilers. Restricting the selection to dry bottom boilers further reduced the candidate power plants and attendant ashes to 101 in number.

The removal of plants that use wet bottom boilers resulted in omission of several firing types that are used exclusively in wet bottom boilers. The remaining dry bottom firing types were not used as a selection criterion, even though conditions for ash formation vary somewhat with firing type.

Emission Controls

The EIA's Annual Electric Generator Report provides information on the particulate control devices and gaseous control devices that are used at a power plant. With respect to particulate control devices, power plants that collect fly ash using wet particulate scrubbers were removed (resulting in 96 plants remaining for consideration). While the EIA indicates the specific gaseous control devices which are used at a power plant, the level at which these devices are used and their resulting effect on the ash is unclear. Therefore, the type of gaseous emission control devices was not used as a screening criterion, even though this process by type can certainly affect the reactivity and usability of fly ash.

Collecting Samples

After reducing the list of 491 coal-fired power plants, numerous fly ash supply companies were contacted to obtain as many 22.7 kg (50 lb) ash samples as possible from the 96 plants that passed the selection criterion. While most of the companies were excited about the research and willing to help, some were resistant and refused to supply any fly ash samples nor would they provide any additional information about their ashes. Ultimately, ash samples (along with their ASTM C 618 test reports) were collected from 15 power plants primarily in the central United States. These power plants are listed in Table 1 along with selected properties of their fly ash as obtained from ASTM C 618 test reports. For comparison, the Corette ash (prior to mercury emission controls) is included in this Table.

Table 1: Selected Fly Ash Samples and Properties

Power Plant Name	Abbreviation	Location	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Total Alkalies	Available Alkalies
J.E. Corette	CORE	MT	30.30	17.11	5.47	29.62	-	2.50	-	-	-	1.68
Boardman	BDMN	OR	31.91	18.58	6.05	27.41	6.96	2.77	2.48	0.35	2.71	1.19
Columbia	COLU	WI	34.08	18.98	5.90	26.28	5.46	2.12	2.11	0.46	-	-
Crawford	CRAW	IL	33.79	17.77	5.62	25.22	5.50	1.98	3.34	0.54	-	-
Fayette Power Project	FAY	TX	37.85	19.43	5.70	23.32	4.98	1.12	-	-	-	1.28
Grand River Dam Authority	GRDA	OK	36.40	20.21	6.29	26.03	5.31	1.55	-	-	-	1.18
J T Deely	JDLY	TX	36.71	21.03	5.32	25.35	4.53	1.24	1.35	0.44	1.64	-
Jeffrey Energy Center	JEFF	KS	30.07	21.05	6.15	28.46	6.77	1.98	-	-	-	-
Joliet	JOLI	IL	32.27	17.52	5.63	26.14	5.70	2.25	3.56	0.52	-	-
Labadie	LAB	MO	37.18	22.02	6.58	23.60	4.73	1.75	-	-	-	1.32
Laramie River Station	LRS	WY	33.02	18.75	5.78	27.85	6.14	2.11	1.88	0.38	2.13	-
Nebraska City	NEB	NE	36.20	19.20	6.10	25.20	5.00	2.40	-	-	-	-
Pawnee	PAW	CO	31.31	18.22	5.92	28.43	7.27	2.72	2.18	0.31	2.38	-
Rush Island	RUSH	MO	37.58	20.82	5.58	25.74	4.89	0.99	-	-	-	1.13
Scherer	SCH	GA	31.69	17.66	6.40	28.63	6.98	2.27	2.21	0.35	2.44	-
Tecumseh Energy Center	TECU	KS	33.04	22.33	7.87	26.31	4.81	1.53	-	-	-	-

TESTING SAMPLES

Based on past experience with the fly ash from the Corette power plant, existing mix designs and testing procedures, modified as previously found appropriate, were used to determine by experiment the adequacy of the 15 fly ashes collected from other sources for use in 100 percent fly ash concrete. Due to the relatively small amount of available material (22.7 kg (50 lb) of fly ash), the trial batch size was set at 0.0025 m^3 (0.087 ft^3). The selected mix design used a 48 percent fly ash paste by volume. Within the paste, a water-to-cementitious-material ratio (i.e. water-to-fly ash ratio) of 0.22 was used. The aggregate consisted of fine (3 mm (1/8 in minus)) and coarse (3 to 10 mm (1/8 to 3/8 in)) graded recycled glass of assorted colors. The coarse to fine aggregate ratio was 3:1. Concretes made with the Corette fly ash as the sole binder will flash set unless a retarder is used. Borax has been found effective in regulating the set time, notably to provide an adequate window of workability to place the material before it hardens. The borax level was varied as deemed appropriate to control the set time as described below. Previous research by MSU/WTI has shown that various borax levels are required to retard the set time of high-calcium fly ash concretes. As a starting point to determine the retarder dosage requirements and preliminary strengths, mixes were made at 0, 0.5 and 1.0 percent of borax by weight of fly ash for each ash (total 45 mixes).

The 28 day unconfined compression strengths for the concretes prepared as described above are reported in Figure 2. These results are for 100 percent humidity cured 51x102 mm (2x4 inch) cylinders. All but two of the mixes (COLU and JDLY) flash set without borax; hence no strength data was recorded for the majority of non-retarded mixes. Additionally, at 1.0 percent borax, LAB did not set and strength data was not recorded. Consequently, Figure 2 does not report strength for some of the ashes at the 0 and 1.0 percent borax levels. While COLU did not flash set, it had the highest strength at a zero retarder level with strength decreasing as retarder level increased. The JDLY ash showed no significant sign of strength, less than 2.75 MPa (400 psi) at any retarder level, indicating that the ash has low self-cementitious behavior. Low compressive strength, less than 4.83 MPa (700 psi), was also observed for the concrete made with the NEB fly ash, even though the concrete flash set at a zero retarder level.

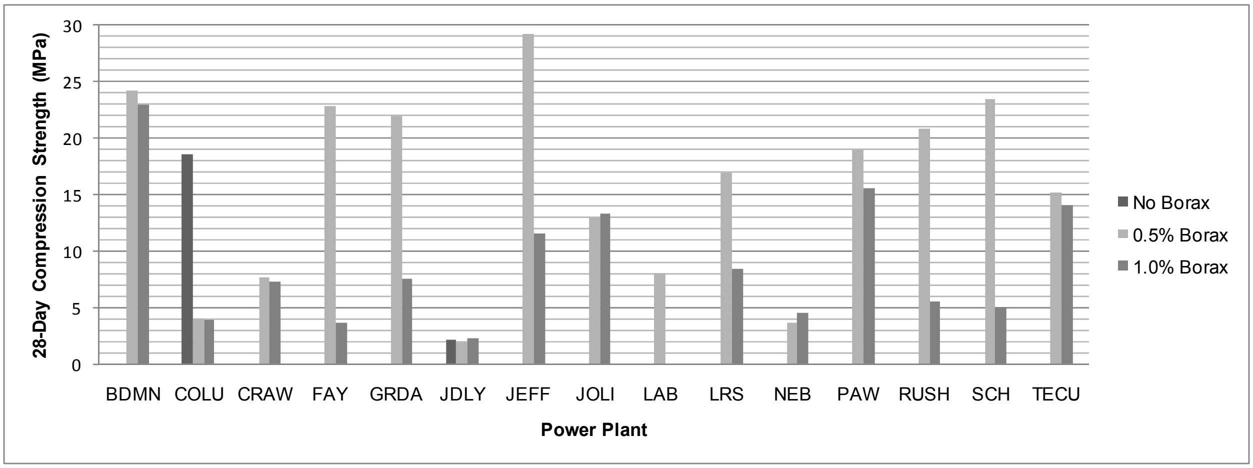

Figure 2: 28-Day Compression Strengths

The retarder dosage had a varying affect on the strength of the fly ash concrete. There was no significant strength difference between the 0.5 percent and 1.0 percent borax levels for concrete made with BDMN, COLU, CRAW, JDLY, JOLI, NEB, and TECU fly ash. The concrete made with PAW fly ash showed moderate strength differences between the 0.5 and 1.0 percent borax levels. Concrete from FAY, GRDA, JEFF, LRS, RUSH, and SCH had much higher 28 day strengths with a 0.5 percent borax level compared with a 1.0 percent borax level.

In this initial screening at borax levels of 0, 0.5, and 1.0 percent, concrete from six of the ashes, BDMN, FAY, GRDA, JEFF, RUSH, and SCH, exceeded a strength of 20.68 MPa (3,000 psi) at 28 days. These ashes were deemed acceptable for general construction applications, as such concretes typically have design 28-day unconfined compression strengths of 20.68 to 27.58 MPa (3,000 to 4,000 psi). The six acceptable concretes were made with ashes from Oregon, Texas, Oklahoma, Kansas, Missouri, and Georgia, indicating that ashes that produce usable strengths are available at relatively diverse locations around the country. Concrete from five of the six ashes only reached strength above 20.68 MPa (3,000 psi) at a 0.5 percent borax level, however, concrete made with BDMN ash had strength exceeding 20.68 MPa (3,000 psi) at both 0.5 and 1.0 borax percentages.

Additional bench top mixes were done using several of the ashes at intermediate retarder levels between 0 and 1.0 percent borax. Varying the borax level improved the compressive strength of the concrete for some of the ashes, which was the case for the LRS and PAW fly ash. At 0.75 percent borax, the LRS ash produced concrete with a compressive strength of 23.58 MPa (3420 psi). At 0.40 percent borax, the PAW ash produced concrete with a compressive strength of 24.61 MPa (3570 psi). Thus, the additional mixes for LR and PAW had higher strengths than the preliminary 0.5 percent borax mixes. As a result of this work, a total of 8 of the 15 ashes in this study achieved compressive strengths exceeding 20.68 MPa (3,000 psi).

SUMMARY AND CONCLUSION

The production of concrete consisting of traditional Portland cement and conventional aggregates has a negative effect on the environment through the emission of greenhouse gasses and the disruption of virgin lands. A twofold environmental advantage can be achieved through using fly ash and glass waste-streams to make concrete instead of conventional materials, that is, issues associated with using virgin materials are voided, and the volume of two significant waste-streams are reduced . This paper provides results of a research effort focused on investigating the use of 100 percent fly ash concrete with glass aggregates. Conclusions drawn from these results include:

- A selection criterion was developed for screening ashes most likely to have self-cementitious properties. This criterion is based on macro-scale factors such as type of coal being burned, combustion process, and emission control technologies.
- Using this selection criterion, 96 plants throughout the US were identified as potential sources of ash capable of being used as the sole binder in concrete.
- Out of these 96 power plants, 15 sample ashes were obtained and tested.
- Over fifty percent of the concretes made with these sample ashes with glass aggregates had compressive strengths suitable for structural/general construction applications (i.e. strength in excess of 20.68 MPa (3,000 psi) at 28 days).

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