Cement-free concrete using alkali-activated high-carbon fly ash as binder

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A Thesis Proposal by

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Abstract

This thesis investigates the use of high-carbon fly ash (HCFA) as a binder material in alkali-activated concretes. Such concretes do not contain Portland cement, and the strength development is attributed to the activation of aluminate and silicate phases in the fly ash using strong alkalis. The alkaline solution-to-fly ash weight ratio, the alkali-activator concentration, and the fly ash content were varied to determine their effects on the compressive strength of the concrete mixture. Preliminary results indicate achievable strengths of over 10 MPa observed after heat curing for 48 hours at 75 °C. Further research will be carried out to improve the compressive strength of such concretes and identify the significant parameters that influence the strength gain. Combination of HCFA along with commonly used Class F fly ash will also be investigated to understand their effects in strength development when subject to alkali activation.

Introduction

Concrete is the most important and widely used construction material in the world. Over 10 billion tons of concrete are produced each year [1]. Concrete is popular due to many reasons. If properly designed and produced, concrete has excellent mechanical and durability characteristics. In general it is moldable, adaptable, relatively fire resistant, widely available, and affordable. Perhaps its most important characteristic is that it can be engineered to satisfy almost any reasonable set of performance specifications.

The production of large quantities of concrete requires extensive amounts of natural resources. The course aggregates such as granite and limestone are mined from the earth, the fine aggregate mainly comes from rivers, and the raw material for cement, limestone, is also mined from the earth [2]. This places a considerable strain on the non-replenishable natural resources. Additionally, the production of each ton of Portland cement releases an equal amount of carbon dioxide into the atmosphere [1]. The production of ordinary Portland cement (OPC) is also very energy intensive.

One of the major means through which the concrete industry tries to achieve the goals of sustainability is through the reduction of cement usage in concrete. Over the last several years, research has uncovered several waste and by-product material from other industries as potential partial cement replacement materials in concrete. The most common waste/by-product materials that have found acceptance in concrete are fly ash which is a residue from coal-burning power plants, ground granulated blast-furnace slag which is a waste product from steel production, and silica fume which is a by-product of the semiconductor industry [3]. The use of these materials in concrete has significant environmental and economic benefits compared to using OPC. One of the primary advantages of these materials over traditional cements from an environmental standpoint is the much lower CO_2 emission rate from their manufacture compared to OPC production [4]. In addition, their use in concrete provides a use for materials which otherwise would be waste products of industry to be disposed of at great cost. Also, the use of these cement replacement materials can improve durability in many cases when compared to OPC concretes [5]. Among these cement replacement materials, fly ash is the most widely used supplementary cementitious material in concrete [1].

Fly ash and slag typically are rich in alumina and silica, while silica fume is purely siliceous. When used as a part of normal concretes, fly ash reacts with the calcium hydroxide produced from cement hydration to form secondary hydration products that result in better material properties. In this project, the aim is to activate fly ash constituents chemically, to produce a material that has binding properties. When activated by alkalis such as sodium hydroxide and sodium silicate, these materials are referred to as geopolymers or alkali-activated cements [3].

Class F materials are generally low-calcium (less than 10% CaO) fly ashes with carbon contents usually less than 5%, but some may be as high as 10%. Class C materials are often high-calcium (10% to 30% CaO) fly ashes with carbon contents less than 2%. Class F fly ash is often used at dosages of 15% to 25% by mass of cementitious material and Class C fly ash is used at dosages of 15% to 40% by mass of cementitious material [5]. The achievable 28-day compressive strengths from these fly ash/cement blended concretes typically range from 25 MPa to 70 MPa [6].

This thesis focuses on the chemical activation of fly ash using sodium hydroxide as the alkali-activator. The alkali activation of fly ash is a chemical process that allows the transformation of glassy structures into very compact well-cemented composites [7]. The main reaction product of alkali-activated fly ash is an alkaline silicoaluminate gel [8]. This thesis will concentrate on the use of HCFA (chemical composition is given in Methodology), which has little published results to support its use in the concrete industry. The alkaline solution-to-fly ash weight ratio, the alkali-activator concentration and the fly ash content are varied to determine their effects on the compressive strength of the concrete mixture.

Alkali-activated Concretes: A Review

Geopolymerisation occurs in alkaline solutions with aluminosilicate oxides and silicates (either solid or liquid) as reactants. Geopolymerisation takes place through a mechanism involving the dissolution of aluminium and silicon species from the surfaces of source materials as well as the surface hydration of undissolved particles [9]. Afterwards, the polymerisation of active surface groups and soluble species takes place to form a gel, generating subsequently a hardened geopolymer structure. In most cases, only a small amount of the silica and alumina present in particles needs to dissolve and take part in the reaction for the whole mixture to solidify.

Many researchers have produced concretes using alkali-activated fly ash that have compressive strengths comparable or superior to those of concrete made with OPC. For example, T. Bakharev [10] created concrete using alkali-activated fly ash with sodium hydroxide (NaOH) and achieved 2-day compressive strength of 10 MPa and 28-day compressive strength of 60 MPa. Another alkali-activator, sodium silicate (Na_2SiO_3), was used to chemically activate fly ash to achieve 2-day compressive strength of 2MPa and 28-day compressive strength of 45 MPa. Another study [9] used Class F fly ashes activated with NaOH from different sources and achieved 28-day compressive strengths of 29-66 MPa. A study by M. Sofia, J.S.J. van Deventerb, P.A. Mendisa, and G.C. Lukey [3] used Class F fly ash with one or more of the following components: sodium carbonate (Na_2CO_3), Na_2SiO_3, and NaOH to achieve 7-day compressive strengths in the range of 35-44 MPa and 28-day compressive strengths of 47-57 MPa.

Researching alkali-activated cements is motivated by the goals of sustainability. Not only do these materials present significant environmental benefits, but they also offer improvements in material properties as well as economic benefits. Current research needs include standards, the development of a larger data base, reactivity and reaction mechanisms, characterization, and processing of raw materials [5]. The development of performance standards will aid in the widespread use of these materials. Generating a more extensive data base will improve predictability in the manufacture and use of alkali-activated cements and enhance the predictability of their performance. Greater understanding of the reactivity and reaction mechanisms such as better defining the activation effectiveness of different types of alkalis will aid in the development of alkali-activated cements. New characterization methods need to be researched because of the variability in composition of many alkali-activated cements. Additional studies are needed to determine the effect of differences in the processing parameters of raw materials.

Despite the availability of results using normal Class F fly ashes, there is a considerable lack of published results indicating the use of high carbon fly ashes, which are generally defined on the basis of having a loss on ignition of greater than 5-6%. Even as normal fly ashes have grown in popularity as research efforts have increased in the last decade, most HCFA is still regarded as a waste material of industrial processes and disposed of at high cost.

There is a significant amount of HCFA produced from circulating fluidized bed combustion (CFBC) of coal. CFBC is preferred to pulverised coal combustion (PCC) because of reduced NO_x emissions. Additionally, SO_2 emissions can be reduced in CFBC if limestone is used as the bed material. PCC generates fly ashes with about 0.5% carbon-in-ash content while CFBC generates fly ases with about 15% carbon-in-ash content [11]. Generally, the fly ash produced form CFBC is regarded as a waste material and lanfilled because of its high-carbon content. If a use for HCFA could be developed, this could aid in sustainability efforts. The aim of this thesis is to publish results in a scientific journal to help generate a use for HCFA in concretes as a complete replacement for OPC or as a blended replacement with normal Class F fly ashes.

Objectives

1. Understand the influence of fly ash dosage and alkali-activator concentration and dosage on the compressive strength of alkali-activated HCFA concrets
2. Optimize mixture proportions for moderate to high compressive strengths

Materials and Experimental Methods

The following table presents the chemical composition of the HCFA used and the chemical composition of a normal fly ash and cement for comparison. The source of the HCFA is the Black River Power Generation Plant.

Table A: Chemical composition of high-carbon fly ash compared to a normal Class F fly ash and cement

	Cement	**Fly Ash (Class F)**	**High-Carbon Fly Ash**
Major Component	**Composition (% by mass)**		
Silicon Dioxide	20.2	59.61	24.05
Aluminum Oxide	4.7	26.55	9.93
Iron Oxide	3	5.39	11.91
Calcium Oxide	61.9	1.57	24.43
Magnesium Oxide	2.6	Not Available	0.94
Sodium Oxide	0.19	Not Available	0.58
Potassium Oxide	0.82	Not Available	1.32
Sulfur Trioxide	3.9	0.1	16.98
Property			
Loss on Ignition (LOI, %)	1.9	2.39	14.66
Fineness (% passing, sieve size)	97.4 (45 μm)	80 (45 μm)	84.6 (45 μm)

High-carbon fly ash was used as the only binder in the concrete mixtures used in this study. Some preliminary mix designs were investigated and based on the resulting compressive strengths certain parameters in the mix design were varied to determine their effect on compressive strength. Among these factors were the alkaline solution-to-fly ash weight ratio, the concentration of the alkali-activator, and the fly ash content.

All mix designs used the same source of HCFA, coarse aggregate, and fine aggregate. The alkali-activator used was NaOH. The HCFA, coarse aggregate, and fine aggregate were mixed when dry to achieve uniformity before adding the alkaline solution and then the additional water was added. Superplasticizer was also used to improve the workability of the concrete. These materials were mixed until uniform and then cast into 2” x 2” x 2” cubes using steel molds.

The concrete was properly vibrated, finished, and then allowed to cure in room temperature conditions for 24 hours. Then the samples were de-molded and heat cured in an oven at 75°C for 48 hours. This duration and temperature have been supported by previous research [9] to deliver the most significant strength gain. Beyond this duration and temperature there is little strength gain achieved [12]. Also curing at elevated temperature for more than 48 hours would not be practical in industry.

Samples were removed 1 hour prior to compressive strength testing to allow them to return to room temperature before testing. Samples were tested using a compressive strength machine and were loaded until failure. From the preliminary results the mix design was altered to investigate the effect certain parameters had on the compressive strength.

Preliminary Results and Discussion

In the first three mix designs the alkaline solution-to-fly ash weight ratio was varied. Compressive strengths were determined using an alkaline solution-to-fly ash weight ratio of 0.40, 0.45, and 0.50. Additional water was required in each of the mixes to make them workable. Addition water-to-fly ash weight ratios of 0.20, 0.10, and 0.10 were used in the first three mixes, respectively. Table B, below, presents these first three mix designs and their respective compressive strengths.

Table B: Preliminary mix designs and compressive strength results

Fly ash (kg/m3 of concrete)	385	396	387
Fine aggregate (kg/m3 of concrete)	756	775	759
Coarse aggregate (kg/m3 of concrete)	859	881	863
Alkaline Solution (kg/m3 of concrete)	**154**	**178**	**194**
Additional Water (kg/m3 of concrete)	**77**	**40**	**39**
NaOH (Molarity)	8	10	8
Superplasticizer content (% by weight of fly ash)	1	1	0
Compressive Strengths (psi)	810.5	590.6*	291.9*
	(broken)	891.9	717.9
	(broken)	1135	679.6
	*not subject to heat curing		

Note that the starred compressive strength values were not subjected to any heat curing, resulting in lower values compared to when the samples were heat cured at 75°C for 48 hours. The highest compressive strengths were achieved with an alkaline solution-to-fly ash weight ratio of 0.45 and an addition water-to-fly ash weight ratio of 0.10. This combination was used in the next few mix designs where the fly ash content and the alkali-activator strength were varied.

In the next few mix designs, the fly ash content was decreased to around 340 kg/m3 of concrete and increased to about 440 kg/m3 of concrete while keeping the proportions of fine aggregate and coarse aggregate used the same. This was conducted at alkali-activator strengths of 6M, 8M, and 10M. Table C, below, presents the next few mix designs and their respective compressive strengths.

Table C: Preliminary mix designs and compressive strength results

Fly ash (kg/m3 of concrete)	**339**	**438**	**337**	**440**	**341**	**443**
Fine aggregate (kg/m3 of concrete)	830	720	833	720	836	723
Coarse aggregate (kg/m3 of concrete)	943	815	948	819	950	822
Alkaline Solution (kg/m3 of concrete)	153	197	152	198	154	199
Additional water (kg/m3 of concrete)	34	44	34	44	34	44
NaOH (Molarity)	**6**	**6**	**8**	**8**	**10**	**10**
Superplasticizer (% by weight of fly ash)	1	1	1	1	1	1
Compressive Strengths (psi)	1620	1161	832.1	944.5	1572	1119
	1419	685.1	1194	1067	1646	1251
	1431	1098	1508	1213	1198	1044

In general, increasing the alkali-activator concentration caused an increase in the compressive strength. A noticeable increase in compressive strength is observed when the fly ash content is decreased to around 340 kg/m3 of concrete at each of the alkali-activator strengths in comparison to increasing it to around 440 kg/m3 of concrete.

Future Work

Future mix designs will be used to investigate the alkaline solution-to-fly ash weight ratio with some of the better performing mixes, such as fly ash content of 340 kg/m3 of concrete of and 10M alkali-activator strength. Decreasing the fly ash content lower than 340 kg/m3 of concrete and using a stronger alkali-activator concentration will be investigated to determine whether this will result in greater compressive. In addition, it has been discussed to use blends of HCFA with a normal Class F fly ash. This will be investigated at a later date after the possibilities of using HCFA as the only binder in concretes has been investigated. After strength optimization, the specific mechanisms that influence strength gain will be investigated using methods such as thermal analysis, X-ray diffraction, electron microscopy, and/or micrographs. Some relevant aspects to examine are what causes the activation and how the presence of sulfates affects it. It is hypothesized that ettringite formation results in extra strength gain, but when the sulfates run out, mono-sulfate forms which results in a loss of strength. A timeline for the completion of this thesis project is presented on the next page.

Timeline

Fall 2008	Thesis topic and mentor selection; begin literature review
January 2009	Become familiar with appropriate laboratory safety, materials, equipment, and procedures with the help of graduate students Deepak Ravikumar and Hieu T. Cam
February 2009	Determine compressive strength of HCFA concretes using varying alkaline solution-to-fly ash weight ratio, alkali-activator concentration, and fly ash content
March 2009	Continue optimizing mix design for compressive strength; complete thesis proposal by March 13
April 2009	Explore combination of HCFA with a normal Class F fly ash; Complete as many strength tests as possible before leaving for summer recess; mix best performing samples and leave to cure over the summer to determine long-term strength; complete progress report due April 24
Summer 2009	Continue literature review, complete draft of Chapters 1-3 of thesis, begin analyzing results
August 2009 – September 2009	Complete necessary remaining mixes and determine compressive strength; begin investigating chemistry behind strength gain
October 2009 – November 2009	Finish necessary lab tests, analyze results, and make conclusions; complete draft of Chapters 4-6 of thesis, begin reviewing thesis
December 2009	Complete first draft of thesis due
January 2009 – February 2009	Finish any necessary lab work and make necessary revisions to thesis; work on submitting results to professional journal(s)
March 2009	Final draft of thesis due (approved by mentor); thesis oral presentation at end of month
April 2009	Final thesis due

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