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Subject: Final Report Entitled "Using Class C Fly Ash to Mitigate Alkali–Silica Reactions in Concrete"

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USING CLASS C FLY ASH TO MITIGATE ALKALI–SILICA REACTIONS IN CONCRETE

CBRC Project Number: 05-CBRC-W04

Final Report

(for the period of July 01, 2006, through June 30, 2008)

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Using Class C Fly Ash to Mitigate Alkali–Silica Reactions in Concrete

ABSTRACT

This project was initially designed as a 3-year study to perform a comprehensive evaluation of assessing the use of Class C fly ash on the effects of alkali–silica reactivity (ASR) in concrete. The intent of the first year effort was to increase the list of industry sponsorship, to perform a literature review on the latest laboratory testing, and to set up a laboratory testing matrix using industry-sponsored cement and fly ash samples. The second and third years were designated for all laboratory testing. Because of the elimination of Combustion Byproducts Recycling Consortium (CBRC) funds, for these last 2 years, the work scope for this U.S. Department of Energy project and final report was modified to only reflect Year 1 goals. The remaining laboratory effort will continue on but with only industry sponsor support.

A very comprehensive and diverse group of industry sponsors was successfully assembled for this project. They include Boral Material Technologies Inc., Western Region Ash Group, Holcim (US) Inc., Lafarge North America Inc., WE Energies, Nebraska Ash Company, Ash Grove Resources, and Mineral Resource Technologies Inc. From these industry sponsors, there have been selected 14 fly ash samples and two cement sources for laboratory testing. In addition, a medium reactive aggregate has also been chosen.

There were mainly three ASTM International (ASTM) methods for evaluating expansion because of the ASR. The first is ASTM C1260, “Potential Alkali Reactivity of Aggregates (Mortar-Bar Method),” and is probably the most widely used test method. Another commonly used test method is ASTM C1293, “Determination of Length Change of Concrete Due to Alkali–Silica Reaction.” A more recent specification, ASTM C1567, “Determining the Potential Alkali–Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method),” addresses ASR mitigation using supplementary cementitious material such as fly ash.

For the laboratory effort, it was decided to use ASTM C1567 for the bulk of the testing. Some of the samples tested under this method will also be evaluated using the concrete method ASTM C1293 but at a reduced effort than was originally designated.

TABLE OF CONTENTS

Using Class C Fly Ash to Mitigate Alkali–Silica Reactions in Concrete

INTRODUCTION

Current utilization rates of fly ash (American Coal Ash Association, 2004) are 28 million tons annually or roughly 40% of what is produced, which still remains a significantly low number. By far the most common application remains the production of portland cement concrete. In order to increase the utilization rate, the need will be to increase the current rate allowable as a partial cement replacement in concrete in addition to finding new uses. Allowing the use of Class C fly ash, and at larger dosages to mitigate alkali–silica reactions (ASR), will assist in meeting this objective

High-calcium fly ashes, classified as Class C by the ASTM International (ASTM) C618 definition, are often excluded as a means to mitigate ASR in concrete because a relationship between high calcium content and expansion was documented when Class C fly ash was used at a 10% to 15% replacement level in concrete. It is generally true that low replacement levels (<15%) of Class C fly ash may not offer ASR mitigation; however, it has been demonstrated that Class C fly ashes can mitigate the effects of ASR at higher replacement levels than specified. In some cases, the amount of Class C fly ash needed to control ASR may exceed specification limits set by state Departments of Transportation. The specific objective of this project is to evaluate higher replacement levels of Class C fly ash in concrete for ASR mitigation and enhanced concrete performance.

ASR is a historic issue in concrete durability. It has been highlighted by discussions within the ASTM C 9.24 subcommittee on Supplementary Cementitious Materials and in conclusions of a paper published by the American Concrete Institute (ACI) Materials Journal (Malvar et al., 2002) that Class C fly ashes containing >10% CaO should not be used to mitigate ASR. While Malvar and others (2002) recommend the use of Class F fly ash, there are areas of the country where Class F fly ash is not readily available, but Class C fly ash is available. In these areas, a large market for fly ash will be lost. It is important to address Dr. Malvar’s conclusions in order to maintain concrete markets for Class C fly ash.

EXECUTIVE SUMMARY

In 2006, the University of North Dakota Energy & Environmental Research Center (EERC) and its partners, the University of Texas at Austin Concrete Materials Laboratory and the University of New Mexico Civil Engineering Department, proposed to perform a multiyear investigation to evaluate the performance of several Class C fly ashes (>10% CaO) using existing predictive ASR test methods. ASTM standard methods are to be applied to fly ash samples and cast specimens produced using varying levels of Class C fly ashes. In addition to these empirical tests, the EERC will evaluate specimens using advanced electron microscopy techniques to look at the mineralogy of the ash and the aggregates and, especially, the reaction products. It is anticipated that results will confirm limited unpublished work that indicates the efficacy of using higher percentages of Class C fly ash to mitigate ASR when using moderately reactive aggregates.

During the first year of this project, Combustion Byproducts Recycling Consortium (CBRC) funding was rescinded because of changes in the U.S. Department of Energy focus for funding energy-related research. This multiyear project had to be changed to a single year effort by modifying the original statement of work. Efforts for Years 2 and 3 will be continued, with support from the industry sponsors, but with a reduced scope of work from the original CBRC proposal. No laboratory testing was performed during the first year activity reported here. The consultants were also dropped from the budget after the first year activities.

The updated work tasks included assembling a consortium of industry supporters with as many participants as possible. Each of the members will be able to furnish samples and be an integral part of developing the program test matrix. In addition, a selection of the best available method(s) to evaluate the impact of fly ash mitigation will also be determined in this updated task.

A very comprehensive and diverse group of industry sponsors was successfully assembled for this project. They include Boral Material Technologies Inc., Western Region Ash Group, Holcim (US) Inc., Lafarge North America Inc., WE Energies, Nebraska Ash Company, Ash Grove Resources, and Mineral Resource Technologies Inc. Between all of these companies, we will be testing 14 types of fly ash using two cement sources. All members have been contacted in regard to fly ash sources and are currently in the process of sending in samples. To date, the EERC has received three fly ashes and one cement source.

There were mainly three ASTM methods for evaluating expansion because of alkali-silica reactivity. The first is ASTM C1260, "Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)," and is probably the most widely used test method. Another commonly used test method is ASTM C1293, "Determination of Length Change of Concrete Due to Alkali–Silica Reaction." A third and more recent specification, ASTM C1567, "Determining the Potential Alkali–Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)," addresses ASR mitigation using supplementary cementitious material such as fly ash.

For the laboratory effort, it was decided to use ASTM C1567 for the bulk of the testing. Some of the samples tested under this method will also be evaluated using the concrete method ASTM C1293 but at a reduced effort than was originally designated.

EXPERIMENTAL

There were mainly three ASTM methods for evaluating expansion because of alkali–silica reactivity. The first is ASTM C1260, "Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)," and is probably the most widely used test method with equivalents in American Association of State Highways and Transportation Officials (AASHTO) (T303) and Canadian Standards Association (CSA) (A23.2-25A). Another commonly used test method is ASTM C1293, "Determination of Length Change of Concrete Due to Alkali–Silica Reaction" (also with AASHTO and CSA equivalents).

A high degree of variability exists in the results of these and several other tests used to predict ASR. Admixtures such as fly ash may be deemed acceptable by one test method but not the other (Mullings and Lobo, 1998; Rogers, 1998; Whiting, 1998; Thomas and Innis, 1998) but often not by both. ASTM C1293 involves making concrete prisms and measuring expansion for 1 year, with the sample being kept at a constant temperature and humidity. The ASTM C1260 procedure is an accelerated version of ASTM C1293 and uses a mortar bar rather than concrete prisms and a Na(OH) solution to accelerate the alkaline environment.

Recent specifications, ASTM C1567, "Determining the Potential Alkali–Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)," addresses ASR mitigation using supplementary cementitious material such as fly ash.

The Energy & Environmental Research Center (EERC) will use a new electron backscattered diffraction system (EBSD) that will allow researchers to determine both the chemistry and mineralogy of a single particle as small as 1 µm in diameter. This means that any phase with some atomic structure (crystallinity) may be identified by its diffraction pattern as with x-ray diffraction but on a particle-by-particle basis rather than a bulk sample. Using the EBSD system, the EERC will document and ultimately gain a reasonable understanding of the relationship between fly ash mineralogy and ASR mitigation with a specific focus on high-calcium ashes.

The EERC will demonstrate the importance and role of mineralogy by examining several mortar bars prepared according to ASTM C1260, ASTM C1567 (the Accelerated Mortar-Bar Method test), and ASTM C1293. Several of the mortar bars and concrete prisms will be examined in detail using the scanning electron microscope with energy-dispersive x-ray system (EDS) for chemical determination. This will be coupled with the EBSD system that will allow the visualization of a particle, the chemical composition as determined by EDS analysis, and the mineralogy of the particle based on the chemistry and crystalline structure. In this manner, a better understanding of the mechanisms of ASR and ASR mitigation will start at a molecular level, and attempts to describe the contribution from aggregate, cement, and fly ash will be made.

RESULTS AND DISCUSSION

A very comprehensive and diverse group of industry sponsors was successfully assembled for this project. They include Boral Material Technologies Inc., Western Region Ash Group, Holcim (US) Inc., Lafarge North America Inc., WE Energies, Nebraska Ash Company, Ash Grove Resources, and Mineral Resource Technologies Inc. Between all these companies, we will be testing 14 types of fly ash using two cement sources. All members have been contacted in regard to fly ash sources and are currently in the process of sending in samples. To date, the EERC has received three fly ashes and one cement source. In addition, a medium-level reactive aggregate is being furnished by one of the sponsors. There is no laboratory testing during this first year of the project. All laboratory testing will be performed in Years 2 and 3.

The proposed mix proportions and test matrix will include the following replacement levels:

- Class C fly ash – 30%, 40%, and 50%
- Class F fly ash – 20% and 35%
- Class C/F blends – 20% and 30%

A review of the available literature clearly indicates that there is still no clear mechanism causing expansion because of ASR. Several test methods have been developed to predict whether or not a particular aggregate or combination of aggregate and cement paste will cause ASR expansion.

Expansion caused by a reaction of the alkali contained in cement and the aggregate in concrete have been noted since the early1940s, primarily in the southwestern United States but also noted in Kansas, Nebraska, Alabama, and Georgia. Studies of these failed concretes showed that the expansion was because of a reaction between the alkali in the cement and the siliceous aggregates used in the concrete. Since then, many studies have been performed to better understand the mechanisms causing the expansion because of ASR and ways to mitigate those reactions.

A review of available literature indicates that no one mechanism has been clearly identified as the cause of expansion because of ASR. A summary of available test methods and advantages and disadvantages was presented by Chang-Seon, Sarkar, and Zollinger (2002) from Texas A&M University. A paper in the ACI (Malvar and others, 2002) states that Class C fly ash is not recommended for ASR mitigation based on limited studies of low-level Class C fly ash concrete showing failures. Dunstan (1981) found low replacement rates of high-calcium ashes resulted in expansion, but expansion decreased with increased fly ash additions. Styron and others (1997) reported effective ASR mitigation when 25% of high-alkali cement was replaced with Class C fly ash.

Lenke and Malvar (2005) report that there are three characteristics of a fly ash that determine its efficiency in preventing ASR: fineness, chemistry, and mineralogy. Several have reported that the finer the fly ash, the better at reducing ASR (Malhotra and Rameanianpour, 1994; Ravina, 1980; Berube et al., 1995; Obla et al., 2003). The chemistry of the fly ash has also been used as a predictor for ASR mitigation (Shehata and Thomas, 2000; Malvar and Lenke, 2005; Malvar and Lenice, 2005) with success. The mineralogy of fly ash is a bit more difficult to use as a predictor for several reasons but has been shown to be important in many areas of fly ash utilization. Lenke and Malvar (2005) and Malvar and Lenice (2005) report that high-calcium fly ashes are less effective in binding alkalies, and hence, there may be some relation between efficiency because of mineralogy and chemistry, which may be partially captured in a chemical relationship. A chemical index was derived characterizing the fly ash and cement based on its chemical constituents, which was optimized to maximize the correlation with expansion test data.

In order to capture a relationship between chemistry and mineralogy, bulk chemical analyses are used in conjunction with bulk mineral analyses, and any excess amount of a particular element is then often considered to be associated with an amorphous phase. Fly ash mineralogy is very complex, with each individual fly ash sphere representing a precursor mineral from which it was formed and whatever inorganic compounds it may have come into contact during formation. Each individual sphere can represent a completely different precursor mineral and may or may not have reached complete melting during its formation. Some minerals are more heat-resistant than others and are not completely incorporated into any melt (quartz), and others have a very low melting temperature (clay minerals) and are in a liquid phase at some point. The time it takes for a fly ash particle to cool will also have some effect on the outcome of the mineralogy. Just as in huge geologic features, certain minerals will crystallize before others, depleting the availability of some elements in the melt to form other phases.

The mineralogy is often the catalyst for reactivity in fly ashes. Some of the Class C ashes found primarily in the western United States have been found to contain various forms of calcium and aluminum phases which are highly reactive when hydrated. These reactions are often exothermic and can create enough heat to cause more reactions to take place. Knowing these phases are present in a fly ash can make a large difference in the behavior of a material which cannot really be predicted by chemistry alone. The addition of just H_2O will cause a large number of reactions that will completely change the physical properties, appearance, and behavior of the material without changing the chemistry.

There were mainly three ASTM methods for evaluating expansion because of alkali-silica reactivity. The first is ASTM C1260, “Potential Alkali Reactivity of Aggregates (Mortar-Bar Method),” and is probably the most widely used test method. Another commonly used test method is ASTM C1293, “Determination of Length Change of Concrete Due to Alkali–Silica Reaction.” A third and more recent specification, ASTM C1567, “Determining the Potential Alkali–Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method),” addresses ASR mitigation using supplementary cementitious material such as fly ash.

There have been numerous research efforts using all three of these standard test methods. Some evaluations were made using only ASTM C1260. McKeen et al. (2000) concentrated on evaluating different sources of local aggregates and fly ashes. While Rogers (1999) evaluated the procedure itself using a multi-interlaboratory study. Shon et al. (2002) evaluated the procedure using variable water/cement ratios and variable curing times.

Comparisons of ASTM C1260 and C1293 (Touma et al., 2001), evaluated several sources of aggregates and how the results compared to mortar bars versus concrete prisms. Later comparisons were made for methods C1260 and C1567 (Lenke and Malvar, 2005) to further refine a piece-wise linear model to better address the actual behavioral relation between the ASR expansion and chemical properties of the fly ash–cement blend.

For this laboratory effort, it was decided to use ASTM C1567 for the bulk of the testing. Some of the samples tested under this method will also be evaluated using the concrete method ASTM C1293 but at a reduced effort than was originally designated. The EBSD system will still be utilized to document and ultimately gain a reasonable understanding of the relationship between fly ash mineralogy and ASR mitigation with a specific focus on high-calcium ashes.

CONCLUSION

Though this project had to be trimmed down from its original concept, the first year activities were still achieved as proposed. At the time of the original proposal, there were only three industry sponsors, and now, that list has grown to seven. The group represents a very knowledgeable list of companies very familiar with alkali-silica reactivity and its effects on concrete durability. The sponsors contributions in samples and guidance will attribute to the projects success.

An evaluation of existing literature on the topic of ASR has helped in focusing the needed laboratory effort for the next two years of this research effort. Much of the laboratory work will be conducted using the standard test method ASTM C1567. A selected ash sample from each sponsor will also be evaluated using the concrete prism method ASTM C1293. The EBSD will also be a useful tool to evaluate fly ash mineralogy and ASR mitigation.

The proposed mix proportions and test matrix will include the following replacement levels:

- Class C fly ash – 30%, 40%, and 50%
- Class F fly ash – 20% and 35%
- Class C/F blends – 20% and 30%

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