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

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ABSTRACT

High-calcium fly ashes, classified as Class C by ASTM International (ASTM) C618 definition, are often excluded as a means to mitigate alkali–silica reactions (ASR) in concrete. This is because a relationship between high-calcium content and expansion was often 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. For highly reactive aggregates, the required dosage of Class C fly ash may be quite high, resulting in reduced early strengths. In some cases, the amount of Class C fly ash needed to control ASR may exceed specification limits set by state Department of Transportations. In these instances, combining Class C fly ash with silica fume, for example, can help to mitigate ASR and improve early strength gain.

The University of North Dakota Energy & Environmental Research Center has completed the second year of a 3-year series of investigations to evaluate the performance of several Class C fly ashes (>10% CaO) using existing predictive ASR test methods. ASTM standard methods were applied to fly ash samples and cast specimens produced using varying levels of Class C fly ashes. The results have confirmed limited and unpublished work that indicates the effectiveness of using higher percentages of Class C fly ash to mitigate ASR when using moderately reactive aggregates.

Results indicate that all the Class C fly ashes submitted for this study helped reduce the expansion of the mortar mixtures, even at the lowest replacement level of 15%. This reduction in expansion continued as the fly ash content increased.

INTRODUCTION

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 industry sponsorship, perform a literature review on the latest laboratory testing, and 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. Year 2 was devoted to mortar bar testing, while Year 3 will be dedicated to concrete testing for ASR. Both of these testing programs will be discussed in detail later in this report.

There are eight contributing members to the ASR consortium: Holcim (US) Inc.; Nebraska Ash Company; Ash Grove Resources; WE Energies; Lafarge North America; Mineral Resources Technologies; Boral Materials Technologies, Inc.; and the Western Region Ash Group. All member contacts for this project are listed in Appendix A. These members have combined to submit 13 fly ash and two cement samples. Ten of the fly ashes are Class C, and the other three are Class F. The fly ashes will only be referred to as FAC-1–10 and FAF-1–3. The fly ash blends and cement sources will be identified as FAB and CEM, respectively. The blends have been produced and tested, but the end results will not be available for another 2 weeks after the time this report is due to the U.S. Department of Energy. A second Year 2 final report will be prepared for the consortium members shortly after the final data is obtained.

Three primary ASTM International (ASTM) methods for evaluating expansion as a result of ASR were used. The first, ASTM C1260 entitled "Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)," 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 Year 2 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 for Year 3.

LITERATURE REVIEW

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 has been noted since the early 1940s, primarily in the southwestern United States but also 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 as a result 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 and others[1] from Texas A&M University. A paper in the American Concrete Institute journal 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.[2] Dunstan[3] found low replacement rates of high-calcium ashes resulted in expansion, but expansion decreased with increased fly ash additions. Styron and others[4] reported effective ASR mitigation when 25% of high-alkali cement was replaced with Class C fly ash.

Lenke and Malvar[5] 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.[6–9] The chemistry of the fly ash has also been used as a predictor for ASR mitigation[5, 10, 11] 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[5] and Malvar and Lenice[11] report that high-calcium fly ashes are less effective in binding alkalies; 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 their 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 formed and whatever inorganic compounds it may have come into contact with 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). 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 that 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 that 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 have been numerous research efforts using the three standard test methods: ASTM C1260, C1293, and C1567. Some evaluations were made using only ASTM C1260. McKeen et al.[12] concentrated on evaluating different sources of local aggregates and fly ashes, while Rogers[13] evaluated the procedure itself using a multi-

interlaboratory study. Shon et al.[14] evaluated the procedure using variable water/cement ratios and variable curing times.

In a comparison of ASTM C1260 and C1293, Touma et al.[15] evaluated several sources of aggregates and how their results compared for mortar bars versus concrete prisms. Lenke and Malvar[5] compared Methods C1260 and C1567 to further refine a piecewise linear model to better address the actual behavioral relationship between ASR expansion and the chemical properties of the fly ash–cement blend.

BACKGROUND

Current utilization rates of fly ash[16] 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 ASR, will assist in meeting this objective

ASR is a reaction between alkali hydroxides in portland cement and siliceous phases present in the admixtures and aggregates composed of SiO_2. Problems with expansion arise when soluble silica reacts with the alkalis forming an alkali–silica hydrate gel, which exhibits directional growth (swells in one direction) and keeps CaO from entering the complex. CaO in the alkali–silica gel does not expand. In concrete, CaO is associated with silica and forms a nonswelling calcium silicate hydrate gel during hydration as a key reaction related to cementation. It has been proposed that CaO deficiency coupled with high alkali in localized areas, such as on aggregate surfaces, or extremely high concentrations of soluble silica allows the alkalis to react with the silica by "diluting" the CaO, leaving sites open for alkali incorporation. Recently, Lenke and Malvor[5] developed a piecewise linear two-parameter model for predicting the fly ash required, to mitigate ASR based on the chemistry of the fly ash, the chemistry of the cement, and the reactivity of the aggregate. Identifying the susceptibility of an aggregate to the ASR reaction before using it in concrete is one of the most efficient practices for preventing ASR damage.[15]

Fly ash is often added to mitigate expansion as a result of ASR. Current thought on the leading mechanisms for which fly ash controls expansion are that the fly ash dilutes the alkali content in the cement. Some of the alkalis are removed from the pore solution by binding them into CaO–silica hydrate gels. The fly ash reduces the concrete permeability and diffusivity by the silica reacting with the $Ca(OH)_2$ produced by the hydration of the cement to form calcium silicate hydrate. Since the calcium silicate hydrate takes up more space than the $Ca(OH)_2$, the pore systems become finer and less continuous. The reduced porosity limits the ability of the alkalis to migrate and, therefore, reduces the ability of alkali–silica gel to form.[17] Thomas[18] indicated that several fly ash concrete samples show little or no expansion even when the available alkali content is relatively high.

The impact of this technology will be in the area of higher replacement levels of Class C fly ashes in concrete in areas where ASR is problematic. Within the U.S. Department of Defense, 23 Air Force, three Army, and six Navy/Marine airfields have reported ASR problems.[19] Several state highway departments have specifications for admixtures to mitigate ASR as do several federal agencies and state Departments of Transportation. Recent survey studies[20] indicated that often only Class F fly ash is identified as suitable for ASR mitigation. This conclusion is often reached because of the limited research available using Class C fly ashes. Although other nonash materials may also mitigate ASR, they are generally more expensive than fly ash.

While there is data available that shows a correlation between ASR and CaO content, the data shows that higher replacement levels of high CaO containing fly ashes can also mitigate expansion because of ASR. By providing adequate data on the use of several Class C fly ashes and associated ASR testing, it is expected that it will be shown that higher replacement levels of high-calcium fly ash can be used to effectively mitigate ASR. In turn, it is expected that the end users requiring ASR protection will gain a comfort level in using Class C fly ash in areas where reactive aggregates are commonly used in concrete.

Almost all fly ashes can be used to prevent damaging expansion as a result of alkali–silica reaction provided they are used in sufficient quantity.[21] It is not really correct to say that some fly ashes do not work—they just do not work when an insufficient quantity is used. The amount of fly ash required depends on the reactivity of the aggregate, the quantity of alkalis contributed by the portland cement, and the composition of the fly ash.

More than 50% Class C fly ash may be required with some aggregates. The pozzolanic reaction that occurs when fly ash is used with portland cement produces a calcium silicate hydrate (C-S-H) that has a lower Ca/Si ration than the C-S-H produced by the hydration of portland cement. C-S-H with a low Ca/Si ration has a greater capacity to bind alkalis, thereby reducing the alkalis available for reaction with the aggregate. Low-calcium Class F fly ash produces C-S-H with a lower Ca/Si ration than high-calcium fly ash, and consequently, more alkalis are bound when Class F fly ash is used.

Preventing and mitigating alkali–silica reactivity in portland cement concrete pavements and structures is the focus of a new $10 million Federal Highway Administration[22] (FHWA) initiative. The 4-year ASR program was established and funded be the 2005 Safe, Accountable, Flexible, Efficient Transportation Equity Act: A Legacy for Users. FHWA held an ASR Benchmarking Workshop in June 2006 in Chicago, Illinois, to gather stakeholder input on the new ASR program. Workshop attendees discussed the current state of the practice and areas where further development and deployment of ASR prevention, identification, and mitigation techniques are needed. Participants noted, for example, that the field identification of ASR is difficult and that there is a lack of understanding of the extent of the problem, as ASR is not included as part of most regular pavement or bridge inspection programs. Inspectors need a test for easy, fast, and reliable identification. Participants noted the need as well for a fast reliable test

method to identify the potential for ASR to occur in concrete mixtures proposed for transportation structures. Workshop participants also stressed the importance of increasing awareness of ASR among agencies and contractors and improving the decision-making process for preventing ASR in new construction.

EXPERIMENTAL PROCEDURES/METHODOLOGIES

ASTM C1260, "Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)," is probably the most widely used test method with equivalents in AASHTO T303 (American Association of State Highway and Transportation Officials) and CSA A23.2-25A (Canadian Standards Association). Recent specifications, ASTM C1567 entitled "Determining the Potential Alkali–Silica Reactivity of Combination of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)," address ASR mitigation using supplementary cementitious material such as fly ash.

Another commonly used test method is ASTM C1293, "Determination of Length Change of Concrete Due to Alkali–Silica Reaction." Since 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 but often not by both.

RESULTS

During this second year of activity, all the fly ashes and fly ash blends were evaluated for ASR using ASTM C1567 standard test method. Both sources of cement were used in this evaluation. The first cement source (CEM-1) utilized fly ash replacement levels of 15%, 30%, 40%, and 50% for the Class C fly ashes and 15%, 30%, and 40% replacement levels for Class F fly ashes. Fly ash replacement levels for CEM-2 were 20%, 30%, and 40% for the Class C fly ashes and 20% and 35% for the Class F fly ashes. The results for both cement sources are indicated in Table 1. The samples are arranged by decreasing levels of calcium oxide content.

The expansion results of the fly ash blends are given in Table 2. As mentioned earlier, the results on the fly ash blends were not available at the time this report was due. The goal was to blend one Class C fly ash source from each of the industry sponsors to produce a blended fly ash with the combined CaO content of between 14% and 16%. Each Class C fly ash tested was blended with one single Class F fly source labeled as FAF-1. This source of Class F ash had the lowest level of CaO of all the samples submitted.

The expansion of each cement control sample are represented in Table 1. For CEM-1, the average 14-day expansion was 0.211%, while the average expansion for CEM-2 is 0.218%. According to ASTM C1260, the expansion of less than 0.10% at 16 days after casting are indicative of innocuous behavior in most cases. In addition, expansions of more than 0.20% are indicative of potentially deleterious expansion and expansions between 0.10% and 0.20% include both aggregates that are known to be innocuous

and deleterious in field performance. Thus both cement sources produce results that are indicative to potentially deleterious expansion.

DISCUSSION AND RECOMMENDATIONS

It is stated in ASTM C1567 that the combination of cement, fly ash, and aggregate that expands less than 0.10% at 16 days after casting is likely to produce acceptable expansions when tested in concrete and have a low risk of deleterious expansion when used in concrete under field conditions.

The expansion results, using CEM-1, indicate that all ten Class C fly ashes helped to reduce the expansion of the mortar mixtures, even at the lowest replacement level of 15%. This reduction in expansion continued at the remaining cement replacement levels, with smaller reductions seen from the 40% to 50% replacement level. In all cases of the Class C fly ashes, tested here using CEM-1, the specimens reached the <0.10% expansion limit at the partial cement replacement level of 40%.

Though the expansion of CEM-2 was less than that of CEM-1, the use of fly ash was not as pronounced in reducing expansion for CEM-2. In some cases (FAC-9 and FAC-3), not all Class C fly ashes reduced the expansion of the mortar mixture at its lowest replacement level of 20%. For these same two Class C fly ashes, the final expansions were not below the 0.10% limit as specified in ASTM C1567. The total alkali contents for CEM-1 and CEM-2 were 0.56% and 0.51%, respectively. There was not that much of a difference between total alkali contents of the two cement sources.

FUTURE ACTIVITIES

As originally designed, the future concrete work (ASTM C1293) will remain intact and begin after the mortar bar testing. A comparison of concrete ASR expansion to mortar bar ASR expansion is an important part of this project's original objectives.

Table 1. Final 14-day Expansion Results for ASTM Test Method C1567-07 (results are all Class C and Class F fly ashes and two cement sources)

Sample Source	FAC-4	FAC-9	FAC-10	FAC-8	FAC-3	FAC-2	FAC-7	FAC-5	FAC-6	FAC-1	FAF-3	FAF-2	FAF-1
SiO_2, %	33.7	37.9	38.8	38.6	42.0	35.8	42.9	44.0	38.9	46.5	60.7	57.8	51.3
Al_2O_3, %	17.9	18.4	18.2	18.0	18.4	20.4	19.5	20.0	18.6	19.7	18.1	26.5	22.2
Fe_2O_3, %	4.94	5.91	5.35	5.61	5.71	6.3	5.76	5.03	4.94	4.26	4.11	4.28	16.06
Total, %	56.54	62.21	62.35	62.21	66.11	62.50	68.16	69.03	62.44	70.46	82.91	88.58	89.56
CaO, %	26.5	24.2	24.2	24.2	23.7	23.7	20.6	18.6	18.5	18.3	10.9	7.0	3.6
SO_3, %	3.29	2.2	1.44	1.69	1.11	2.61	0.97	1.92	3.62	1.97	0.0	0.0	0.75
MgO, %	6.52	5.23	4.82	4.97	4.23	4.14	4.1	4.16	4.31	3.46	2.38	1.46	1.14
Na_2O, %	2.62	2.1	1.97	2.19	2.16	2.64	1.86	2.1	6.35	0.1	0.95	0.29	0.6
K_2O, %	0.45	0.48	0.6	0.63	0.64	0.45	0.66	0.8	0.75	0.5	0.84	1.03	2.73
Ash Level	CEM-1, 14-day expansion = 0.211%, average of four tests, ASTM C1260-07												
15%	0.155	0.187	0.186	0.189	0.183	0.191	0.119	0.122	0.162	0.174	0.118	0.016	0.063
30%	0.129	0.125	0.122	0.112	0.122	0.102	0.064	0.049	0.113	0.090	0.039	0.015	0.012
40%	0.052	0.086	0.073	0.082	0.087	0.049	0.033	0.034	0.066	0.035	0.022	0.012	0.008
50%	0.043	0.045	0.034	0.049	0.057	0.032	0.016	0.014	0.043	0.028			
Ash Level	CEM-2, 14-day expansion = 0.218%, average of two tests, ASTM C1260-07												
20%	0.180	0.209	0.181	0.197	0.197	0.163	0.152	0.122	0.175	0.148	0.121	0.016	0.052
30%	0.119	0.185	0.144	0.138	0.177	0.123	0.091	0.082	0.123	0.091			
35%											0.019	0.009	0.012
40%	0.052	0.112	0.071	0.073	0.133	0.086	0.047	0.028	0.064	0.029			

Table 2. Final 14-day Expansion for All Fly Ash Blends Using CEM-1

Class C Fly Ash Source	FAB-1 FAC-9	FAB-2 FAC-8	FAB-3 FAC-3	FAB-4 FAC-2	FAB-5 FAC-5	FAB-6 FAC-6
Fly Ash C Amount, %	60	60	50	60	75	75
FAF-1 Amount, %	40	40	50	40	25	25
SiO_2, %	43.3	44.0	42.2	41.4	46.1	42.4
Al_2O_3, %	19.9	19.6	20.2	21.3	20.5	19.6
Fe_2O_3, %	10.01	9.83	10.54	10.14	7.87	7.89
Total, %	73.21	73.43	72.94	72.84	74.47	69.89
CaO, %	15.8	15.8	15.0	15.9	14.6	14.3
SO_3, %	1.63	1.23	2.12	1.92	1.47	2.77
MgO, %	3.71	3.5	3.9	3.1	3.51	3.53
Na_2O, %	1.57	1.57	1.62	1.92	1.78	4.89
K_2O, %	1.37	1.45	1.59	1.31	1.26	1.27
Ash Level	CEM-1, 14-day expansion = 0.211%, average of four tests, ASTM C1260-07					
20%						
35%						

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