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ABSTRACT

Strict regulations on emission of undesirable gases (SO_x and NO_x) into the atmosphere is expected to result in increasing amounts of low-quality coal combustion by-products (such as clean-coal ash) from power plants. Maximum recycling of such by-products is very important for sustainable developments in energy and construction industries. This paper presents the results of a laboratory investigation for the use of high-volume clean-coal ash on mitigating alkali-silica reaction expansion. Up to 80% cement was replaced with a combination of clean-coal ash and Class C or Class F fly ash. A proprietary activator was used to activate the hydration of the blends. The potential alkali-silica reaction of the blends was determined according to modified ASTM C 227 mortar bar method. Test results indicated that all the blends with coal ash had lower expansion than the control mixture with Type I cement at test ages up to 91 days. ASR expansion decreased with the increasing amount of clean-coal ash. The addition of chemical activator increased ASR expansion.

Key words: Activators; ASR; fly ash; clean-coal ash; CCPs

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INTRODUCTION

Alkali-silica reaction (ASR) is the chemical reaction between the hydroxyl ions in the pore water within concrete and certain type of rock minerals. Its detrimental expansion was first recognized in 1940 [1]. It is generally agreed that for ASR to take place and to cause damage, all the three members of the “Triad” must be present, namely, sufficient alkali in concrete, critical amount of reactive aggregate, and sufficient moisture [2]. Numerous experimental investigations have shown that addition of Class F fly ash is an effective method to mitigate the deleterious effects of ASR. Using Pyrex glass as reactive aggregate, Dunstan [3] evaluated the effectiveness of 17 conventional Class C or Class F fly ashes on ASR. He concluded that a low-calcium oxide content ash generally produced smaller expansion compared to high-calcium oxide content ash. However, it was also reported that the available alkali content of the ash, instead of calcium oxide content, is the key factor in controlling ASR. When the available alkali content of the ash is greater than 1.5%, there is a pessium limit [4]. In a study of the performance of twelve fly ashes in the accelerated mortar bar test (ASTM C 1260), Thomas [5] found that the expansion at 14 days linearly increases with the ratio of $(\text{Na}_2\text{O} + \text{CaO})/\text{SiO}_2$.

Due to more stringent environmental regulations and increasing use of low-grade coal, the number of coal-fired power plants with flue gas desulfurization (FGD) systems is growing and is anticipated to grow significantly higher. Spraying of a sorbent is one type of these systems. In this process, for example, slaked lime slurry is sprayed as fine mist into the flue gas in a reaction vessel where the atomized slurry reacts with SO_2 from the flue gases and forms calcium sulfite. A small portion of the calcium sulfite is further oxidized to form calcium sulfate. In addition to sulfite and sulfate, the solid by-product

collected by this process contains a high portion of fly ash particles coated with sulfite and sulfate, and minor amount of un-reacted lime. The sulfite and sulfate formed from the SO₂ are deposited on the surface of the fly ash particles [6]. Due to its high content of sulfite/sulfate, the utilization rate of such ash (a.k.a. clean-coal ash) is much lower than conventional Class C or Class F fly ash. A recent research indicated that with a proper chemical activator, high-volume clean-coal ash could be used in blended cements [7]. Furthermore, concrete prepared from such blended cements showed superior properties to Type I portland cement [8].

This paper deals with the effects of chemical activator and high-volume clean-coal ash on ASR expansion tested according to modified ASTM C 227.

EXPERIMENTAL PROGRAM

Materials

ASTM Type I cement, Class C fly ash, Class F fly ash, and clean-coal ash were used as cementitious materials in this study. Their chemical composition and physical properties are shown in Table 1 and Table 2, respectively. A previously tested and evaluated proprietary activator was selected as the chemical activator. Crushed glass was used as reactive aggregate.

Preparation of Cementitious Blends

Three series of cementitious blends were proposed for this study. In Series C, 40% to 80% of Type I cement was replaced by Class C fly ash and clean-coal ash. 2% to 4% activator was added to activate the reaction of these cementitious materials. In Series F, the same amount of Type I cement was replaced by Class F fly ash and clean-coal ash.

The mixture proportion of Series N was the same as Series C except that chemical activator was not added. The details of mixture proportion are shown in Table 3. For each mixture listed in Table 3, Type I cement together with Class C or Class F fly ash, clean-coal ash, and chemical activator were blended in a ball mill (charged with ceramic balls) for five minutes. Chemical analysis results indicated that this procedure yielded a uniform blend. The resulting blends were used for preparation of ASR expansion specimens.

Experiment Design

ASR expansion was tested according to modified ASTM C 227, Standard Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar Bar Method). 25 x 25 x 285-mm mortar bars (four for each concrete mixture) containing crushed glass as reactive aggregate were prepared according to ASTM C 227. To accelerate alkali-silica reaction, after two days of curing the specimens were immersed in 1.0 N sodium hydroxide solution at 80 °C as described in ASTM C 1260. Length of the specimens was measured at ages up to three months.

TEST RESULTS AND DISCUSSIONS

The linear expansion of mortar bars in 1.0 N alkali solution is plotted in Fig. 1. For the control mixture, expansion started in the first two days of immersion and increased rapidly thereafter. At all test ages the expansion of the control mixture was higher than the mixtures with fly ash. For mixtures with Class C fly ash, clean-coal ash, and chemical activator (Series C) the expansion started in the first week and increased rapidly after 10 days of immersion. The expansion decreased with increasing amount of

Class C fly ash and clean-coal ash. For mixtures with Class F fly ash, clean-coal ash, and chemical activator (Series F), the trend of expansion was similar as the mixtures in Series C. However, at the same fly ash content, the expansion of Series F mixtures was significantly lower than that of Series C mixtures. It is noted that with 80% Class F fly ash and clean-coal ash (Mixture F3), the mortar bars did not show significant expansion even after three months immersion in alkali solution.

ASTM C 1260, Standard Test Method for Potential Alkali Reactivity of Aggregate (Mortar-Bar Method) states: “because the specimens are exposed to NaOH solution, the alkali content of the cement is not a significant factor in affecting expansion.” However, from Fig.1 it is clearly noticed that the alkali content being incorporated into the mixture as chemical activator had a dramatic effect on expansion of mortar bars. For example with 40% fly ash content, the 14-day expansion decreased from about 0.1% for Mixture C1 to less than 0.01% for Mixture N1 (Fig. 2), and the 56-day expansion decreased from more than 0.7% for Mixture C1 to about 0.25% for Mixture N1 (Fig. 3). This trend is even more prominent for mixtures with 80% fly ash (14-day & 56-day, Fig. 2 & Fig. 3), Mixtures C3 vs. N3.

This phenomenon may be contributed to pozzolanic reaction, which was accelerated when specimens were immersed in hot (80°C) alkali solution. During pozzolanic reaction, alkali cations might be incorporated in the hydration products, thus less alkali available for alkali-silica reaction [9]. It is believed that alkalis are incorporated within the interlayer of the CSH phase mostly by neutralizing SiOH groups. Amount of alkali hydroxide incorporable increases with decreasing CaO/SiO₂ mole ratio [10]. Pozzolanic reaction also reduces pore size and permeability of mortar bars;

therefore, the external alkali in the solution takes more time to penetrate to the inside of the specimens. It was suggested that the limit for alkali in blended cement to be 1.2% equivalent Na_2O [10]. It will have the same performance as 0.6% equivalent Na_2O for portland cement [11].

CONCLUSIONS

1. Clean-coal ash together with Class C or Class F fly ash can significantly reduce ASR expansion. The expansion decreased with increasing amount of these mineral admixtures.
2. Alkali chemical activator increased ASR expansion compared to mixtures without chemical activator.
3. Pozzolanic reaction consumes alkali, reduces pore size, and mobility of the alkali, thus reduces ASR expansion.

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Table 1 - Chemical composition of cementitious materials

Composition	Type I cement	Class C fly ash	Class F fly ash	Clean- coal ash
SiO ₂ , %	18.5	35.0	48.7	27.5
Al ₂ O ₃ , %	4.3	18.5	27.5	15.1
Fe ₂ O ₃ , %	2.8	5.4	6.4	3.0
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ , %	--	58.9	82.6	45.6
CaO, %	67.9	27.7	8.2	26.4
MgO, %	1.6	5.5	1.8	3.6
TiO ₂ , %	--	1.4	1.3	0.5
SO ₃ , %	2.3	2.4	0.5	19.7
Na ₂ O + 0.658K ₂ O, %	0.6	3.7	1.7	1.1
Moisture Content, %	0.4	0	0.1	0.2
Loss on Ignition, %	1.7	0.2	3.2	2.2

Table 2 - Physical properties of fly ashes

Properties	Test results			ASTM C 618		
	Class C fly ash	Class F fly ash	Clean-coal ash	N	F	C
Density, g/cm ³	2.69	2.41	2.52	--	--	--
Fineness, m ² /kg, by air permeability test method	435	3450	950	--	--	--
Fineness, amount retained on No. 325 sieve, percent	5.2	23.6	2.4	≤ 34	≤ 34	≤ 34
Strength activity index:						
with portland cement, at 7 days, percent of control	99	73	101	≥ 75	≥ 75	≥ 75
with portland cement, at 28 days, percent of control	102	81	107	≥ 75	≥ 75	≥ 75
Water requirement, percent of control	93	102	95	≤ 115	≤ 105	≤ 105
Soundness: autoclave expansion or contraction, percent	0.1	-0.02	0.01	≤ 0.8	≤ 0.8	≤ 0.8

Table 3 – Proportions of cementitious blends

Mixture	Type I cement	Class C fly ash	Class F fly ash	Clean-coal ash	Na ₂ SO ₄
C1	60%	20%	--	20%	2%
C2	40%	30%	--	30%	2%
C3	20%	20%	--	60%	4%
F1	60%	--	20%	20%	2%
F2	40%	--	30%	30%	2%
F3	20%	--	20%	60%	4%
N1	60%	20%		20%	--
N3	20%	20%		60%	--

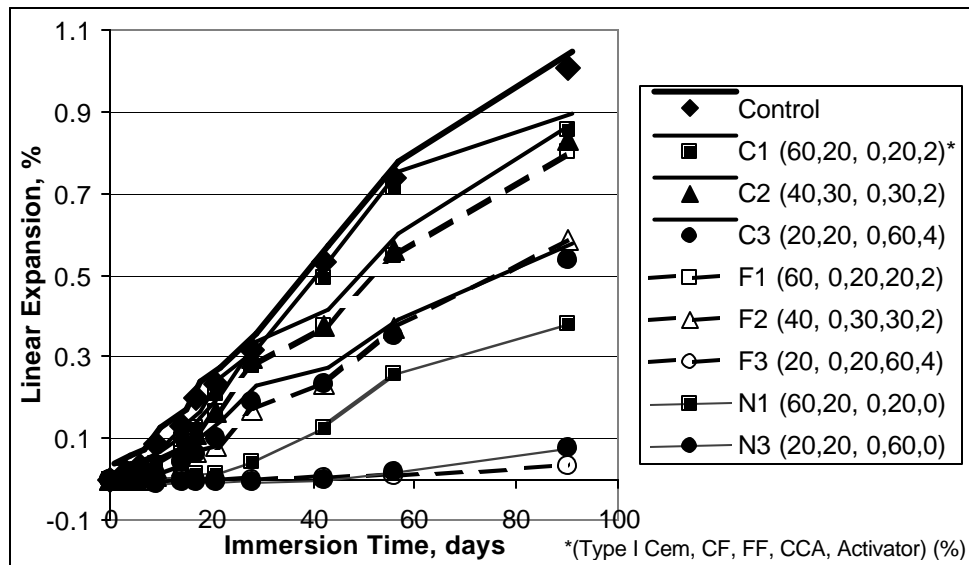


Fig. 1 – Linear expansion of mortar bars

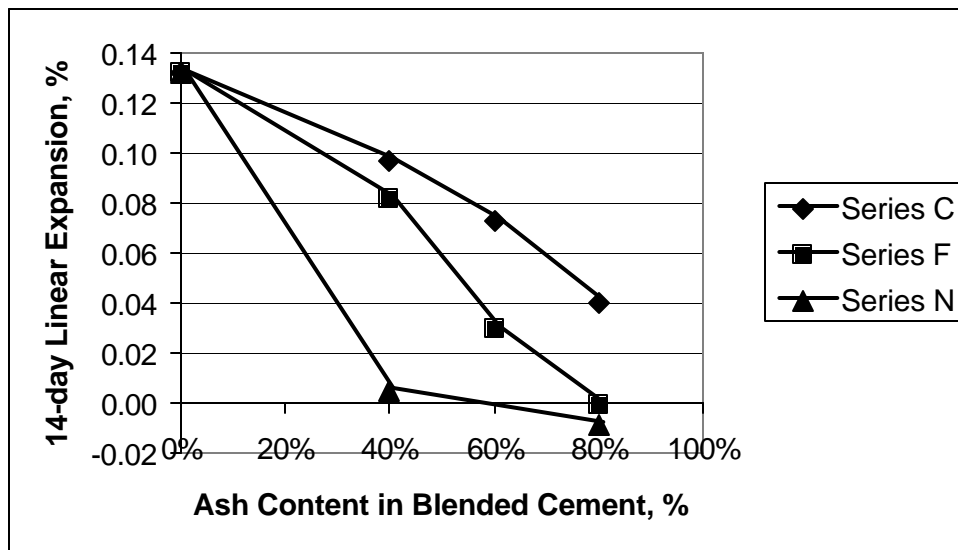


Fig. 2 – 14-day expansion versus fly ash content

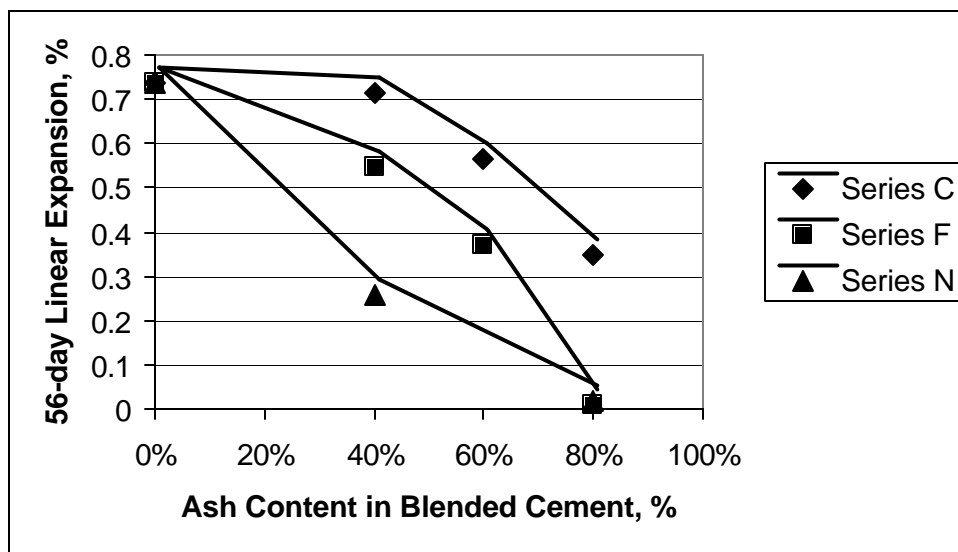


Fig. 3 – 56-day expansion versus fly ash content