

Efficiency of Fly Ash in Mitigating Alkali-Silica Reaction Based on Chemical Composition

by L. Javier Malvar and Lary R. Lenke

While recent specifications address alkali-silica reaction (ASR) prevention using recycled products, such as fly ashes, as cement replacement, the restrictions on the ashes may be too conservative. Data from previous research studies were used to assess the effectiveness of fly ashes in preventing ASR based on their chemical composition, the composition of the cement, and the reactivity of the aggregates. A chemical index was derived to characterize the fly ash and cement based on their chemical constituents. For the fly ashes, this index correlated well with ASTM C 618 and CSA A3001 classifications. This index was also used to assess the efficiency of ashes that did not meet either specification. For a given ash, cement, and aggregate reactivity, it was possible to derive the minimum cement replacement that is needed to ensure, with 90% reliability, that the 14-day ASTM C 1260 (modified, or C 1567) expansion would remain below 0.08%.

Keywords: admixtures; alkali-silica reaction; durability; fly ash.

INTRODUCTION

A recent state-of-the-art review (Malvar et al. 2002) resulted in the development of guidelines to prevent alkali-silica reaction (ASR), which are now used by the Tri-Services (U.S. Navy, Air Force, and Army) for airfield pavements, and are being exported into Department of Defense (DOD) unified facilities guide specifications dealing with concrete in general. These guidelines, however, are somewhat conservative, allowing only the use of ASTM C 618 Class F fly ashes with additional restrictions. Hence, various ashes very close to, but not meeting, that specification cannot be used, in some cases increasing concrete costs by requiring the transportation of other ashes from far away. The objective of this paper is to refine the fly ash requirements using their chemical composition, and to provide an alternate classification to ASTM C 618 that would allow ash assessment as well as the usage of ashes currently not meeting that specification.

RESEARCH SIGNIFICANCE

Public Law 106-398 (2001) directs the Secretary of Defense to explore available technologies to prevent, treat, or mitigate ASR. To date, 32 DOD airfields have reported ASR problems. The costs are staggering: as an example, the Air National Guard Channel Islands Site concrete apron was built in 1989 and replaced in 2003 at a cost of \$16 million. While recent specifications now address ASR prevention using recycled products such as fly ash as cement replacement, the restrictions on the ashes may be too conservative, preventing further savings.

BACKGROUND

Alkali-silica reaction (ASR) is the reaction between the alkali hydroxide in portland cement and certain siliceous

rocks and minerals present in the aggregates, such as opal, chert, chalcedony, tridymite, cristobalite, and strained quartz. The products of this reaction often result in significant concrete expansion, cracking, and ultimately, failure of the concrete structure, including significant potential for foreign object damage to aircraft (refer to Helmuth et al. [1993] or Thomas [1996] for details on the chemical reactions). Alkali-aggregate reaction (AAR) is the reaction between the cement hydroxides and mineral phases in the aggregates, usually of siliceous origin. In this paper, no distinction is made between AAR and ASR. ASR needs several components to occur: alkali (supplied by the cement, although external sources can exist), water (or high moisture content or humidity), and a reactive aggregate.

There are three characteristics of a fly ash that determine its efficiency in preventing ASR:

- **Fineness**—Finer pozzolans are more efficient in reducing ASR expansion. For example, Malhotra and Ramezani-pour (1994) state “fineness of fly ashes is one of the most important physical properties affecting pozzolanic activity” (refer also to Ravina [1980] and Bérubé et al. [1995]). Ultra fine fly ash (UFFA), with particle sizes around 3 μm , is very effective despite a slightly higher CaO content of approximately 11.8% (Obla et al. 2003). Raw silica fume, with particle sizes of approximately 0.1 μm , is also very effective in preventing ASR.
- **Mineralogy**—While ashes can be characterized by their basic chemical components, these components can be bound differently and react differently from ash to ash. For example, Mehta (1986a) showed the importance of mineralogy in mitigating sulfate attack.
- **Chemistry**—This approach has already been used with success (Shehata and Thomas 2000; Thomas and Shehata 2004) and constitutes one starting point of the current investigation (Malvar et al. 2003; Malvar and Lenke 2005; Lenke and Malvar 2005).

In general, for a given ash, the chemical composition is easily obtained, but not the fineness (except for its compliance with ASTM C 618) or its mineralogy. If all ashes studied conform to ASTM C 618, the variation in fineness between them will be limited (except for a few exceptions), and this factor will not be very useful in differentiating between ashes. In the following correlations, only the chemical composition is used: each chemical constituent of the fly ash

ACI Materials Journal, V. 103, No. 5, September-October 2006.

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and cement is weighted based on their relative percentages (by weight) in the blend, and their molar equivalent. In addition, each chemical constituent, or group thereof, can be weighted using an additional factor (for example, α and β described as follows), which would also carry information on the reactivity (itself perhaps a partial reflection of mineralogy) of the constituent or constituent group. This may explain why previous models based solely on chemical analysis have provided good correlations (for example, Shehata and Thomas [2000] and Thomas and Shehata [2004]).

PREVIOUS TESTS

Data were gathered from five previous research studies addressing the use of fly ash in mitigating ASR. A correlation was sought between the chemical composition of the ash and the cement, and the 14-day expansion per ASTM C 1260 (also called the accelerated mortar bar test [AMBT]). For cementitious blends of cement and fly ash, ASTM C 1260 was typically modified to represent the blend (this is now addressed in ASTM C 1567). Fly ash and cement compositions for all five studies are shown in Table 1 and 2. The 14-day expansions using cement alone, E_{14c} , are stated in the following for each aggregate studied. The 14-day expansions of the cement and fly ash blends, E_{14b} , are available in Table 4 of Malvar and Lenke (2005).

McKeen et al. (1998, 2000) tested five fly ashes with four reactive aggregates and with a single lot of Type I/II low-alkali cement (0.55% $\text{Na}_2\text{O}_{\text{eq}}$, where $\text{Na}_2\text{O}_{\text{eq}} = \text{Na}_2\text{O} + 0.658 \text{K}_2\text{O}$). AASHTO T 303 (similar to ASTM C 1260 or CSA A23.2-25A) was used to determine the 14-day control expansions E_{14c} , which were: 0.417 to 0.534% (Santa Ana aggregate), 0.492 to 0.495% (Mimbres aggregate), 0.799 to 0.801% (Albuquerque Shakespeare aggregate), and 0.785 to 0.806% (Placitas aggregate). The CaO content for the five ashes varied from 3.6 to 24.5%.

Shehata and Thomas (2000) tested 18 ashes (with a CaO content from 5.6 to 30%) with one cement (1.02% $\text{Na}_2\text{O}_{\text{eq}}$) and reactive Spratt aggregate ($E_{14c} = 0.371\%$). Based on the Canadian Standards Association specifications (CSA A3001 2003) (formerly CSA A23.5), the ashes were classified as low-lime Type F ash ($\text{CaO} \leq 8\%$), medium lime Type CI ($8\% < \text{CaO} \leq 20\%$), and high-lime Type CH ($\text{CaO} > 20\%$).

Touma et al. (2000, 2001) evaluated a Type F ash ($\text{CaO} = 12.3\%$) and a Type C ash ($\text{CaO} = 26.1\%$) with six reactive aggregates and one Type I/II high-alkali cement (1.14% $\text{Na}_2\text{O}_{\text{eq}}$). The aggregates expansions E_{14c} were by decreasing reactivity: 0.91% (New Mexico), 0.79% (Idaho), 0.42% (Iowa), 0.29% (Wyoming), 0.17% (South Dakota), and 0.15% (Virginia).

Shon et al. (2004) studied one Type C fly ash ($\text{CaO} = 25.9\%$) with a medium alkali cement (0.65% $\text{Na}_2\text{O}_{\text{eq}}$) using a reactive siliceous sand with $E_{14c} = 0.245\%$.

Detwiler (2003) cites developed data using the 14-day AMBT with low, medium, and high CaO fly ashes (5.7, 18.6, and 25.7%, respectively) and a Type I low-alkali cement

Table 1—Fly ash composition

Fly ash	Study*	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	MgO	Na ₂ O _{eq}	Type [†]
LG	S&T	41.96	19.64	20.07	5.57	0.95	1.19	2.30	F
FM	S&T	47.34	22.34	15.08	6.38	1.43	0.82	1.41	F
MN	S&T	61.50	20.52	4.29	8.68	0.19	1.70	0.56	F
BD II	S&T	45.66	21.42	5.53	12.34	0.84	2.76	8.45	F
SD I	S&T	50.92	23.46	4.62	13.63	0.23	0.86	3.77	F
SD II	S&T	51.56	22.90	4.58	15.15	0.28	1.16	2.80	F
TB	S&T	40.68	21.19	4.50	15.87	2.18	3.54	8.46	C
C1	S&T	44.29	20.96	5.23	17.51	2.13	4.21	1.68	F
WM	S&T	39.77	21.46	5.69	18.46	1.86	3.77	4.14	C
BR	S&T	32.71	19.02	5.76	18.85	4.81	4.30	8.73	C
PI	S&T	38.42	20.57	5.64	20.50	1.76	4.39	3.05	C
C2	S&T	39.83	19.56	5.54	21.53	2.14	4.62	1.94	C
EW	S&T	38.22	18.43	5.72	24.61	1.55	4.72	1.68	C
PP	S&T	35.20	18.72	6.06	26.61	2.49	5.12	1.83	C
IN	S&T	36.12	18.64	6.07	26.62	1.80	5.41	1.60	C
OK I	S&T	34.60	16.45	7.13	27.71	2.71	5.89	1.65	C
OK II	S&T	31.65	16.65	7.28	29.10	3.17	6.57	1.85	C
CC	S&T	41.12	11.24	5.93	30.00	2.13	4.40	2.26	C
4-corners (4F)	NM	62.56	25.10	4.68	2.81	0.00	0.81	2.40	F
Coronado (CF)	NM	63.37	22.26	5.34	3.60	0.02	1.06	2.53	F
Escalante (EF)	NM	61.34	25.11	4.42	4.94	0.08	1.09	1.25	F
Esc/Tolk (ET) [‡]	NM	50.19	22.25	4.68	14.73	0.59	3.23	1.67	F
Tolk (TC)	NM	39.04	19.39	4.94	24.51	1.10	5.36	2.08	C
Low CaO (DL)	Detwiler	44.80	23.54	16.98	5.66	1.22	1.26	2.07	F
Medium CaO (DM)	Detwiler	41.00	21.50	6.03	18.62	1.10	4.62	2.25	C
High CaO (DH)	Detwiler	34.68	19.51	5.81	25.74	1.94	6.00	2.35	C
F-Ash (IF)	Touma	56.50	19.30	4.70	12.30	1.50	2.30	0.30	F
C-Ash (IC)	Touma	34.99	20.25	6.24	26.12	1.74	4.65	1.18	C
C-Ash (SC)	Shon	35.20	21.60	5.40	25.90	1.40	4.80	1.20	C
Barber's Point	§	43.47	18.42	6.30	15.72	6.56	1.45	1.40	
UFFA [#]	§	50.66	27.24	3.06	11.80	1.03	2.51	0.35	F

*S&T: Shehata and Thomas (2000); NM: McKeen et al. (2000); Detwiler: Detwiler (2003); Touma: Touma et al. (2001); and Shon: Shon et al. (2004).

[†]ASTM Type.

[‡]50/50 blend of two ashes: Escalante Type F and Tolk Type C.

[§]These ashes were not used in model development but in demonstrating model usage.

^{||}Meets neither Type C nor Type F fly ash specifications.

[#]Ultra-fine fly ash.

(0.43% $\text{Na}_2\text{O}_{\text{eq}}$) using a single reactive quartzite aggregate with $E_{14c} = 0.25\%$.

EFFECT OF EACH CONSTITUENT ON ASTM C 1260 EXPANSION

In the studies considered, straight replacements of cement with fly ash were completed, so that the total cementitious material content remained the same. In the correlations, the total chemical cementitious content, that is, the total amount available from both the ash and the cement, was used for each chemical constituent. To allow for direct comparisons, the expansion of the mixture with a blend of cement and fly ash, E_{14b} , was normalized by the expansion of the mixture with cement only, E_{14c} . The chemical constituents are

Table 2—Portland cement composition and chemical index C_c

Cement type	Study*	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	MgO	Na ₂ O _{eq}	C_c †
High alkali	S&T	20.83	5.11	2.01	62.98	3.25	2.43	1.02	4.17
Low alkali	NM	21.10	4.30	3.20	63.90	3.00	2.00	0.55	3.87
Low alkali	Detwiler	20.87	4.53	2.28	63.99	2.34	3.86	0.43	4.44
High alkali	Touma	20.90	4.43	3.01	62.65	3.06	2.97	1.15	4.32
Medium alkali	Shon	19.12	5.07	3.40	64.73	3.13	0.64	0.65	3.71

*S&T: Shehata and Thomas (2000); NM: McKeen et al. (2000); Detwiler: Detwiler (2003); Touma: Touma et al. (2001); and Shon: Shon et al. (2004).

$$\dagger C_c = \frac{\text{CaO}_{\text{eq}\alpha\text{c}}}{\text{SiO}_{2\text{eq}\beta\text{c}}} = \frac{\text{CaO} + 6.0(0.905\text{Na}_2\text{O} + 0.595\text{K}_2\text{O} + 1.391\text{MgO} + 0.700\text{SO}_3)}{\text{SiO}_2 + 1.0(0.589\text{Al}_2\text{O}_3 + 0.376\text{Fe}_2\text{O}_3)}$$

divided into two groups: those that increase expansion (CaO, Na₂O, K₂O, MgO, and SO₃) and those that reduce it (SiO₂, Al₂O₃, and Fe₂O₃).

Calcium oxide (CaO)

The fly ash content of calcium oxide (or lime) has been shown to have the greatest effect on the efficiency of the ash in mitigating ASR (Malvar et al. 2002; McKeen et al. 2000; Shehata and Thomas 2000). Current DOD guidelines for pavements do not allow Class C fly ash and limit the CaO content of Class F fly ash to 10% (Malvar et al. 2002). The New Mexico State Highway and Transportation Department (2000) places a 10% restriction as well. Canadian guidelines even classify fly ashes based on CaO content (CSA A3001 2003). A good correlation is found between the normalized expansion and the CaO content of the blend with a coefficient of determination $R^2 = 0.71$ (Fig. 1). The CaO content varied from approximately 3 to 30% for the ashes (Table 1), and from approximately 63 to 65% for the cements (Table 2). Because the cement CaO content was fairly constant, the cementitious CaO variation is mostly due to the ash CaO content.

Alkalis (Na₂O and K₂O)

Sodium and potassium oxides have historically been grouped together and their content limited, both in the cement and the fly ash. For reactive aggregates, it is recommended to use low-alkali cement ($\leq 0.6\%$ content per ASTM C 150 [1997]), and for fly ash, the available alkalis are sometimes limited to 1.5% (Malvar et al. 2002; New Mexico State Highway and Transportation 2000). Mixtures with low-alkali cement and ashes and with large variation in the other constituents, however, could be expected to have a low correlation with the ASTM C 1260 14-day expansion, in addition to the low sensitivity of this test to alkalis in the mixture (as indicated under Significance and Use). Thomas and Shehata (2004) found a good correlation between CaO/(SiO₂)² and AMBT expansion independent of alkali content. Similarly, for the ashes studied herein, there was no noticeable correlation between the cementitious alkali content and the normalized expansion (R^2 close to zero). ASTM C 618 (2003) no longer includes the 1.5% available alkali limit as a supplementary optional chemical requirement. For higher alkali content (three of the ashes have more than 8% equivalent alkalis), however, the correlation might be expected to be more significant.

Magnesium oxide (MgO)

AASHTO M 295 (similar to ASTM C 618 and CSA A 23.5) used to require a 5% MgO limit in the fly ash to prevent deleterious expansion from the formation of magnesium

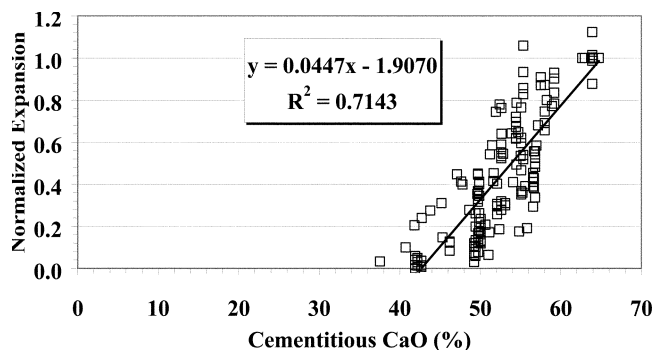


Fig. 1—Effect of cementitious CaO content on 14-day AMBT expansion.

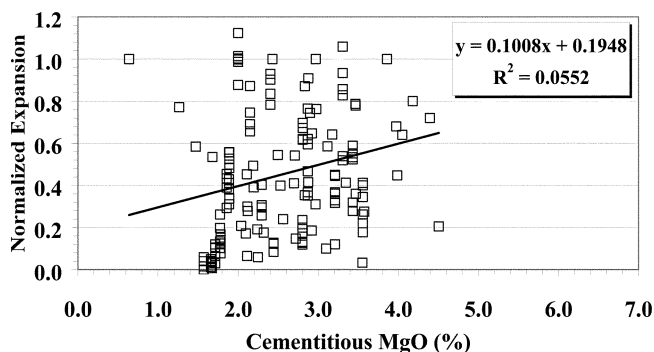


Fig. 2—Effect of cementitious MgO content on 14-day AMBT expansion.

hydroxide (ACAA 1995). This limit is still enforced, for example, by the New Mexico State Highway and Transportation Department (2000). Class F fly ashes typically have very little MgO, but Class C ashes are likely to have more (Malhotra and Ramezani-pour 1994; ACAA 1995; Glauz et al. 1996). Mehta (1986b), however, indicated that the MgO in fly ash often occurs either in noncrystalline form or in the form of nonexpansive melilite phase, so a weak correlation would be expected. Figure 2 shows a very weak correlation between normalized expansion and MgO content.

Sulfur trioxide (SO₃)

Sulfur trioxide is limited to a maximum of 5% in ASTM C 618 for both Class C and F ashes. Klieger and Gebler (1987) state that fly ashes inhibit ASR expansion with the most significant correlations being those with MgO, SO₃, and the ratio CaO/SiO₂. Figure 3 shows a moderate correlation ($R^2 = 0.50$) between normalized expansion and cementitious SO₃ content.

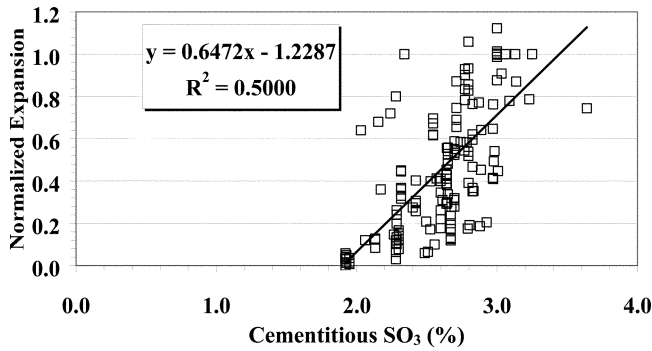


Fig. 3—Effect of cementitious SO_3 content on 14-day AMBT expansion.

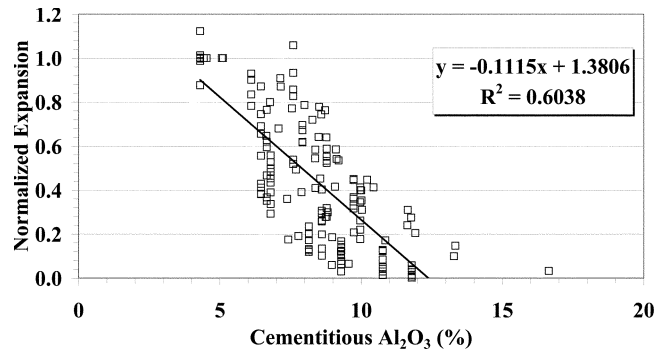


Fig. 5—Effect of cementitious Al_2O_3 content on 14-day AMBT expansion.

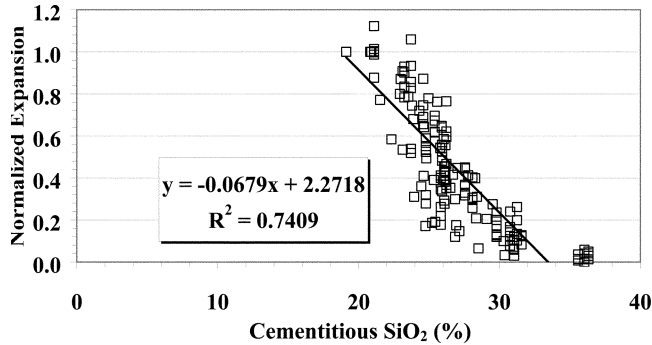


Fig. 4—Effect of cementitious SiO_2 content on 14-day AMBT expansion.

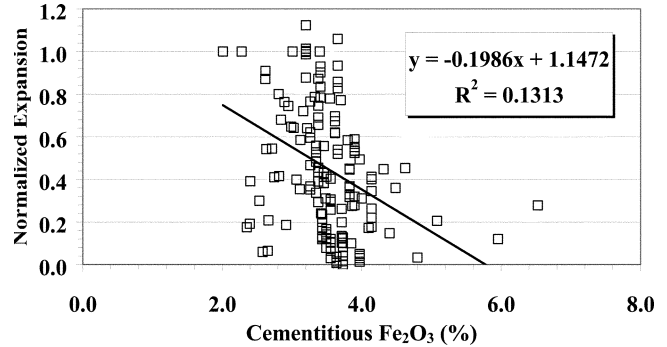


Fig. 6—Effect of cementitious Fe_2O_3 content on 14-day AMBT expansion.

Silicon dioxide (SiO_2)

Silicon dioxide shows pozzolanic activity, that is, forms a cementitious product by reaction with calcium hydroxide (Mehta 1986b). Increased contents of SiO_2 have proven to increase the ash effectiveness and lower the expansion. Figure 4 shows a significant inverse correlation ($R^2 = 0.74$) between the cementitious SiO_2 content and the normalized 14-day expansion.

Aluminum trioxide (Al_2O_3)

Alumina can contribute to the pozzolanic effect of silica, and often the sum $SiO_2 + Al_2O_3$ has shown good correlation with pozzolanic activity (Malhotra and Ramezani-pour 1994). Figure 5 shows the inverse correlation ($R^2 = 0.60$) between normalized expansion and cementitious Al_2O_3 content.

Iron oxide (Fe_2O_3)

Malhotra and Ramezani-pour (1994) report that, for most ashes, the iron oxide is present as nonreactive hematite and magnetite, so a weak correlation would be expected. Some researchers have indicated that including the iron oxide together with the silicon and aluminum oxides did not improve the relationships (Malhotra and Ramezani-pour 1994). Figure 6 shows a very weak inverse correlation ($R^2 = 0.13$) between normalized expansion and cementitious Fe_2O_3 content.

EFFECT OF CONSTITUENT COMBINATIONS ON EXPANSION

Constituents promoting expansion

CaO has been recognized as having one of the most deleterious effects on expansion, and ASR expansion has often been correlated to CaO , or CaO/SiO_2 . Hence, other

deleterious constituents, such as the alkalis, MgO , and SO_3 were replaced by their CaO molar equivalents as

$$CaO_{eq} = CaO + 0.905Na_2O_{eq} + 1.391MgO + 0.700SO_3 \quad (1)$$

If the alkalis were given separately, this would be equivalent to

$$CaO_{eq} = CaO + 0.905Na_2O + 0.595K_2O + 1.391MgO + 0.700SO_3 \quad (2)$$

Figure 7 shows the relation between normalized 14-day expansion and cementitious CaO_{eq} . The correlation ($R^2 = 0.78$) is better than any previous correlation with a single constituent promoting expansion (Fig. 1 to 3) or other combinations thereof (not shown herein).

Constituents reducing expansion

SiO_2 is typically considered the most beneficial constituent in preventing expansion. Hence, the Al_2O_3 and the Fe_2O_3 were replaced by their SiO_2 equivalents

$$SiO_{2eq} = SiO_2 + 0.589Al_2O_3 + 0.376Fe_2O_3 \quad (3)$$

Figure 8 shows a strong inverse correlation ($R^2 = 0.78$) between expansion and cementitious SiO_{2eq} , better than any previous correlation with a single component reducing expansion (Fig. 4 to 6) or other combinations thereof.

Combination of all constituents

The normalized expansion was correlated to the ratio CaO_{eq}/SiO_{2eq} (using Eq. (1) and (3), or (2) and (3)), as

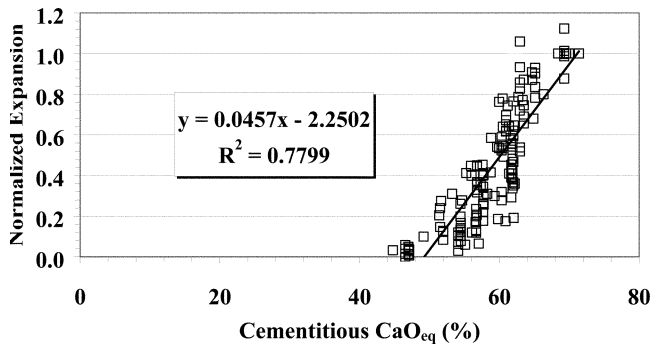


Fig. 7—Effect of equivalent CaO content on 14-day AMBT expansion.

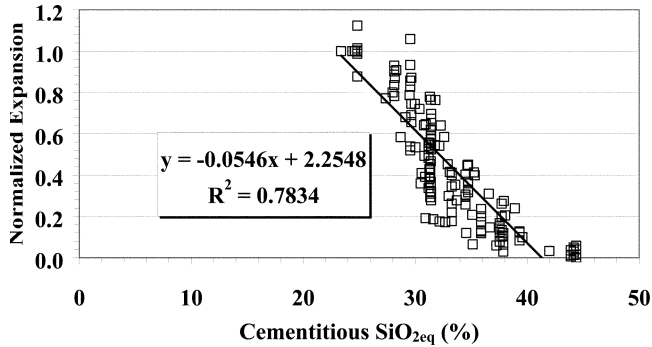


Fig. 8—Effect of equivalent SiO₂ content on 14-day AMBT expansion.

shown in Fig. 9, where the correlation ($R^2 = 0.83$) is an improvement from the correlations with just CaO_{eq} (Fig. 7) or $\text{SiO}_{2\text{eq}}$ (Fig. 8). The blend $\text{CaO}_{\text{eq}}/\text{SiO}_{2\text{eq}}$ was normalized by the cement only $\text{CaO}_{\text{eq}}/\text{SiO}_{2\text{eq}}$ to account for the various cements used.

A better fit is trilinear, with two segments of zero slope at the beginning and end of the data (that is, at low and high replacement levels, as in Thomas and Shehata [2004]). If this trilinear fit is used, Fig. 10 is obtained, with a correlation $R^2 = 0.867$.

To account for different reactivity, chemical constituents can be weighted independently or by groups. Two weighting factors (α and β) were included in the CaO and SiO₂ equivalencies, replacing the previous ratio $\text{CaO}_{\text{eq}}/\text{SiO}_{2\text{eq}}$ with a so-called chemical index for the blend C_b

$$C_b = \frac{\text{CaO}_{\text{eq}}\alpha b}{\text{SiO}_{2\text{eq}}\beta b} = \quad (4)$$

$$\frac{\text{CaO} + \alpha(0.905\text{Na}_2\text{O} + 0.595\text{K}_2\text{O} + 1.391\text{MgO} + 0.700\text{SO}_3)}{\text{SiO}_2 + \beta(0.589\text{Al}_2\text{O}_3 + 0.376\text{Fe}_2\text{O}_3)}$$

where $\alpha = 5.64$ and $\beta = 1.14$ are optimal weighting factors (optimized to maximize R^2). If the normalized expansion is plotted as a function of the normalized cementitious chemical index, C_b/C_c , a figure similar to Fig. 10 is obtained (refer to Malvar and Lenke [2005]) but with the best correlation so far of $R^2 = 0.9026$. For a blend of ash and cement, the CaO blend content would be W times the ash CaO plus $(1 - W)$ times the cement CaO, where W is the weight fraction of the ash

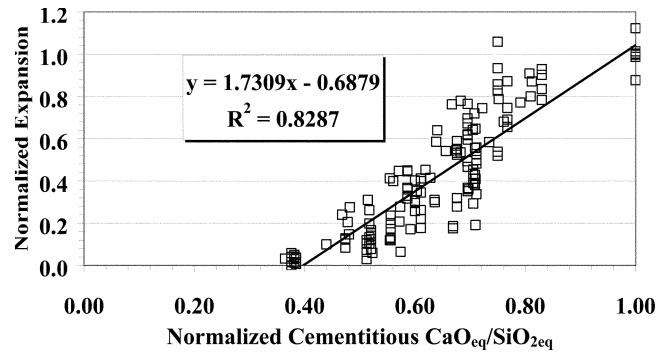


Fig. 9—Effect of normalized $\text{CaO}_{\text{eq}}/\text{SiO}_{2\text{eq}}$ ratio on 14-day AMBT expansion.

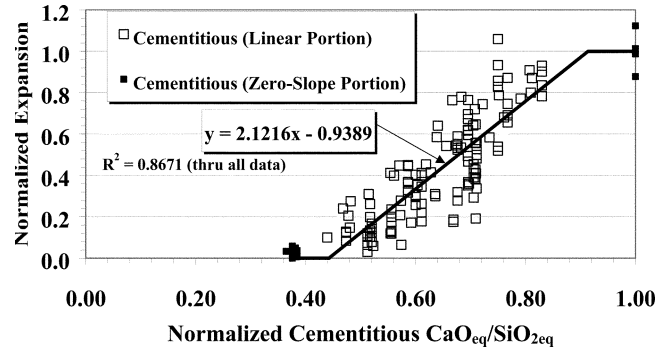


Fig. 10—Effect of normalized $\text{CaO}_{\text{eq}}/\text{SiO}_{2\text{eq}}$ ratio on 14-day AMBT expansion.

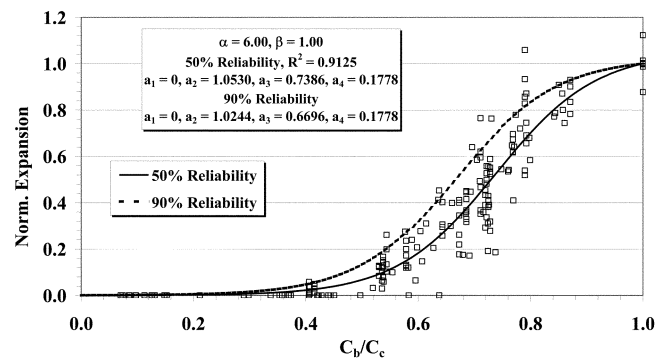


Fig. 11—Effect of C_b/C_c ratio on AMBT expansion (hyperbolic tangent model).

constituent. The same chemical index can be defined for a blend with only cement (0% ash), denoted C_c (Table 2), and for a blend with only fly ash (100% ash), denoted C_{fa} (Table 3).

Finally, the best fit is obtained using a nonlinear hyperbolic tangent model as follows

$$\frac{E_{14b}}{E_{14c}} = \frac{a_1}{2} \left[1 - \tanh \left(\frac{(C_b/C_c) - a_3}{a_4} \right) \right] + \frac{a_2}{2} \left[1 + \tanh \left(\frac{(C_b/C_c) - a_3}{a_4} \right) \right] \quad (5)$$

where $\alpha = 4.42$; $\beta = 0.754$; $a_1 = 0$; $a_2 = 1.0550$; $a_3 = 0.7342$; $a_4 = 0.1834$; and $R^2 = 0.9149$. The value of R^2 does not change

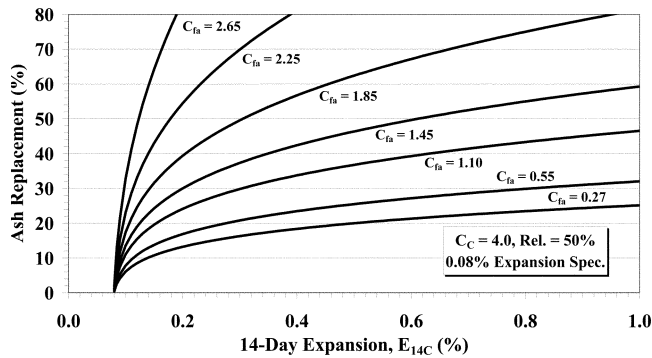


Fig. 12—Minimum fly ash replacement to mitigate alkali-silica reaction with 50% reliability.

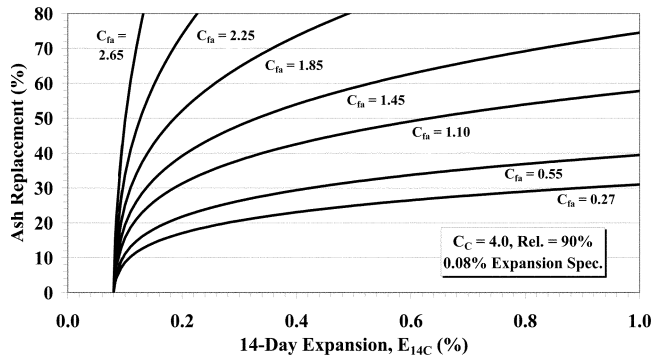


Fig. 13—Minimum fly ash replacement to mitigate alkali-silica reaction with 90% reliability.

significantly for values of α and β near the previous ones, and for simplicity, $\alpha = 6$ and $\beta = 1$ are adopted, with $a_1 = 0$; $a_2 = 1.0530$; $a_3 = 0.7386$; and $a_4 = 0.1778$, yielding $R^2 = 0.9125$, as shown by the solid line in Fig. 11. The values of $\alpha = 6$ and $\beta = 1$ were used to calculate the chemical indexes C_{fa} , C_c , and C_b (for the fly ash, cement, and blend, respectively). Given that ASTM C 1260 indicates in its Precision section “the results of two properly conducted tests in two different laboratories should differ by no more than 27% of the mean expansion,” further increases in R^2 may be difficult to achieve.

Fly ash chemical index

Table 3 classifies all the ashes studied by increasing chemical index C_{fa} . It is seen that a value of $C_{fa} < 1.45$ usually represents an ASTM C 618 Class F ash, and values of $C_{fa} > 1.45$ usually represent a Class C ash. When compared to the Canadian standard (CSA A3001 2003), a value of $C_{fa} < 0.55$ usually represents a Canadian Class F ash, $0.55 < C_{fa} < 1.45$ usually represents a Class CI ash, and values $C_{fa} > 1.45$ usually represent a Class CH ash. Hence, the chemical index C_{fa} has a very good correlation with both standards.

MINIMUM REQUIRED FLY ASH

For a given fly ash, a given cement, and a given aggregate reactivity, the objective is to determine the amount of fly ash for the mixture to be nonreactive. This can be accomplished starting from Fig. 11. The maximum ASTM C 1260 14-day expansion sought is 0.08% (Malvar et al. 2002), and if E_{14c} is the AMBT expansion with cement only, then the maximum normalized expansion sought in Fig. 11 is $0.08/E_{14c}$. Entering $0.08/E_{14c}$ on the y-axis gives a maximum value of C_b/C_c on the

x-axis. Defining the inverse of the hyperbolic tangent function of Fig. 11 as function g yields the following

$$\frac{C_b}{C_c} = g\left(\frac{0.08}{E_{14c}}\right) = a_4 \tanh^{-1}\left(\frac{2(0.08/E_{14c}) - (a_1 + a_2)}{a_2 - a_1}\right) + a_3 \quad (6)$$

However, from Eq. (4)

$$C_b = \frac{\text{CaO}_{\text{eq}\alpha b}}{\text{SiO}_{2\text{eq}\beta b}} = \frac{W(\text{CaO}_{\text{eq}\alpha fa}) + (1 - W)(\text{CaO}_{\text{eq}\alpha c})}{W(\text{SiO}_{2\text{eq}\beta fa}) + (1 - W)(\text{SiO}_{2\text{eq}\beta c})} \quad (7)$$

where W is the percent fly ash substitution by weight (expressed as a decimal), and

$$C_c = \frac{\text{CaO}_{\text{eq}\alpha c}}{\text{SiO}_{2\text{eq}\beta c}} \quad (8)$$

from which the required weight fraction of the ash can be derived as

$$W = \frac{1 - g(0.08/E_{14c})}{\left(1 - \frac{\text{CaO}_{\text{eq}\alpha fa}}{\text{CaO}_{\text{eq}\alpha c}}\right) - \left(1 - \frac{\text{SiO}_{2\text{eq}\beta fa}}{\text{SiO}_{2\text{eq}\beta c}}\right)g(0.08/E_{14c})} \quad (9)$$

This formula gives the minimum required fly ash substitution as a function of three sets of inputs: the ash chemistry (given by $\text{CaO}_{\text{eq}\alpha fa}$ and $\text{SiO}_{2\text{eq}\beta fa}$), the cement chemistry (given by $\text{CaO}_{\text{eq}\alpha c}$ and $\text{SiO}_{2\text{eq}\beta c}$), and the 14-day AMBT expansion with cement only, E_{14c} . These inputs can also be used to find the cement chemical index C_c using Eq. (8), and the fly ash chemical index C_{fa} , using Eq. (7) with $W = 1$. Once C_{fa} and C_c are calculated, and assuming that a single cement is used (C_c constant), W can be plotted as a function of E_{14c} and C_{fa} . This is shown in Fig. 12 for a cement with chemical index $C_c = 4.0$. In this figure, the first four curves ($0.27 \leq C_{fa} \leq 1.45$) represent ASTM C 618 Class F ashes ($C_{fa} = 0.27$ represents the most efficient ash in this study). A cement replacement of 25 to 40% using these Class F ashes could mitigate very reactive aggregates, with 14-day expansions of up to 0.4% with the least efficient one, and up to 1% with the most efficient one (ASTM C 1260 indicates that expansions beyond 0.2% are deleterious, and between 0.1 and 0.2% possibly deleterious). Class C ashes with $C_{fa} \approx 1.85$ could mitigate aggregates with expansions of up to 0.2% at 40% replacement. The least effective Class C ashes ($C_{fa} \approx 2.65$) could only mitigate very low-reactivity aggregates. This is still a great benefit—this chart allows the use of some Class C fly ashes for the cases of low or no reactivity.

The minimum replacement from Fig. 12 is based on using the best fit to the data in Fig. 11 (that is, a 50% reliability level). Instead, it is recommended to use a 90% reliability level, represented by the dashed curve in Fig. 11 (with parameters $a_1 = 0$, $a_2 = 1.0244$, $a_3 = 0.6696$, and $a_4 = 0.1778$). This curve was obtained by shifting the 50% reliability curve to the left until 90% of the AMBT data points were to the right of it. When this curve is used, Fig. 13 is obtained, which gives the minimum required replacement with a reliability of 90% that the expansion will be less than the stipulated 0.08%. In Fig. 13, Class C ashes with $C_{fa} \approx 1.85$ can mitigate low reactivity aggregates up to expansions of

0.12% at replacements of 35%. Fly ashes with $C_{fa} \approx 2.25$ can mitigate very low reactive aggregates with up to 0.10% expansion at 35% replacement. Fly ashes with $C_{fa} \approx 2.65$ could only be used with innocuous aggregates.

Figure 12 and 13 were developed for a typical cement with $C_c = 4$. For other cements in this study, C_c varied only from 3.71 to 4.44 (Table 2), hence, Fig. 13 could be used as a good approximation to find the minimum replacement for typical cements with 90% reliability.

Although this method can be used to calculate minimum amounts of fly ash cement replacement to mitigate ASR, in general it would be advisable to use absolute minimum replacements depending on the application, whether or not the aggregates are reactive, because the resulting concrete will, in general, be cheaper and more durable. For example, the U.S. Navy requires a minimum of 25% Class F fly ash in pavements independent of reactivity (Malvar et al. 2002), and the New Mexico State Highway and Transportation Department (2000) requires 20% Class F minimum, or 25% Class C minimum if the aggregate is innocuous.

CLASSIFICATION USING CHEMICAL INDEX

As indicated previously, the fly ash chemical index C_{fa} has a good correlation with ASTM C 618. Table 3 shows that only ashes DM and BDII appear reversed compared to the ASTM classification; however, BDII has 8.45% Na_2O_{eq} compared to 2.25% for DM (Table 1).

When compared to the Canadian standard (CSA A3001 2003), the chemical index also shows good agreement, with a couple of exceptions (Table 3). For example, ash MN is a CI but appears within the CSA Type F ashes: this ash has $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 = 86.3\%$ and almost no SO_3 and no alkalis—it is a very good ash, and arguably should be an F ash. CSA actually allows classifying it as an F ash because its CaO content of 8.68% can be considered less than $8 \pm 2\%$ (the Canadian standard states: “For the purpose of classification the tolerance shall be $\pm 2\%$ on the CaO limits”). Fly ashes BR and TB appear within the CH ashes (Table 3) but are classified as CI—this is due to their high contents of MgO and SO_3 , and very high alkalis, in addition to a CaO content near the 20% threshold for CH. Hence, despite their CI classification, they are less efficient in mitigating ASR than several CH ashes. CSA would actually allow classifying BR as a CH ash (because its CaO content of 18.85% can be considered more than $20 \pm 2\%$).

As an additional comparison, the sum of the ASTM-specified oxides ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) is also shown in Table 3. In general, this sum closely follows the chemical index in an inverse fashion (with $R^2 = 0.96$ between them), and therefore this ASTM C 618 sum could be used as an approximate alternative to the chemical index to assess the efficiency of an ash to mitigate ASR (for example, for use in Fig. 13).

The chemical index can also be used to assess additional ashes that do not meet typical standards. For example, in Hawaii, cement is imported and is very expensive. If local ashes could be used to replace cement, this would provide considerable savings. Unfortunately, the available ash at Barbers Point is neither a Type F nor a Type C per ASTM C 618, and is only a Type CI by the Canadian standard. For this fly ash, the chemical index is 1.11, making it equivalent to an ASTM C 618 Class F ash in Table 3. From Fig. 13, at a replacement of 40%, this ash could mitigate fairly reactive aggregates (E_{14c} up to 0.30%). At a 25% replacement level, it could be used with aggregates of low reactivity (E_{14c} up to 0.14%).

Table 3—Fly ash type and chemical index C_{fa}

Fly ash name	Study*	Fly ash chemical index C_{fa}^\dagger	Ash type (ASTM)	Ash type (CSA)	$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3^\ddagger$
Escalante (EF)	NM	0.27	F	F	90.9
4-corners (4F)	NM	0.29	F	F	92.3
Coronado (CF)	NM	0.33	F	F	91.0
MN	S&T	0.36	F	CI	86.3
FM	S&T	0.41	F	F	84.8
Low CaO (DL)	Detwiler	0.50	F	F	85.3
LG	S&T	0.52	F	F	81.7
F-Ash (IF)	Touma	0.57	F	CI	80.5
SD II	S&T	0.62	F	CI	79.0
SD I	S&T	0.63	F	CI	79.2
Esc/Tolk (ET) [§]	NM	0.82	F	CI	77.1
C1	S&T	1.21	F	CI	70.5
Medium CaO (DM)	Detwiler	1.32	C	CI	68.5
BD II	S&T	1.40	F	CI	72.6
WM	S&T	1.47	C	CI	66.9
C2	S&T	1.49	C	CH	64.9
PI	S&T	1.54	C	CH	64.6
EW	S&T	1.55	C	CH	62.4
C-Ash (SC)	Shon	1.57	C	CH	62.2
C-Ash (IC)	Touma	1.60	C	CH	61.5
Tolk (TC)	NM	1.63	C	CH	63.4
CC	S&T	1.76	C	CH	58.3
IN	S&T	1.78	C	CH	60.8
TB	S&T	1.83	C	CI	66.4
PP	S&T	1.85	C	CH	60.0
High CaO (DH)	Detwiler	2.00	C	CH	60.0
OK I	S&T	2.07	C	CH	58.2
OK II	S&T	2.43	C	CH	55.6
BR	S&T	2.66	C	CI	57.5

*S&T: Shehata and Thomas (2000); NM: McKeen et al. (2000); Detwiler: Detwiler (2003); Touma: Touma et al. (2001); and Shon: Shon et al. (2004).

†

$$C_{fa} = \frac{\text{CaO}_{eq\alpha/fa}}{\text{SiO}_{2eq\beta/fa}} = \frac{\text{CaO} + 6.0(0.905\text{Na}_2\text{O} + 0.595\text{K}_2\text{O} + 1.391\text{MgO} + 0.700\text{SO}_3)}{\text{SiO}_2 + 1.0(0.589\text{Al}_2\text{O}_3 + 0.376\text{Fe}_2\text{O}_3)}$$

‡Sum of ASTM specified oxides.

§50/50 blend of Escalante F (EF) and Tolk C (TC).

Another interesting ash is an UFFA (Obla et al. 2003), also shown in Table 1. While the most important characteristic of UFFA is its fineness (well below ASTM C 1260 requirements), its chemical composition includes 11.8% CaO, making it a CI ash in Canada and preventing its usage in some cases. Its fly ash chemical index is 0.57, so that it has the chemistry of a very effective fly ash for ASR mitigation (refer to Table 3), in addition to the benefits of its fineness.

CONCLUSIONS

Data from previous research studies were used to assess the effectiveness of fly ashes in preventing ASR, based on their chemical composition, the composition of the cement, and the reactivity of the aggregates. A chemical index was derived based on the fly ash (or cement) constituents, which was optimized to maximize the correlations with test data. For the fly ashes, this index, C_{fa} , correlated well with ASTM C 618 and CSA A3001 fly ash classifications, and with the sum of ASTM-specified oxides ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$).

This index was also used to assess the efficiency of other ashes that did not meet either specification. For a given aggregate reactivity, a given cement, and a given ash, it was possible to derive the minimum cement replacement that is needed to ensure with 90% reliability that the 14-day AMBT expansion would remain below 0.08%.

ACKNOWLEDGMENTS

The first author was supported by the Naval Facilities Engineering Command mission funding for the Pavement Design Technical Center of Expertise. The second author was supported by the Office of Naval Research and the American Society for Engineering Education Summer Faculty Fellowship Program during his stay at the Naval Facilities Engineering Service Center during the summers of 2004 and 2005.

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