

USE OF FLY ASH IN CONCRETE PAVEMENTS

By:

L. Javier Malvar

Naval Facilities Engineering Service Center

1100 23rd Avenue

Port Hueneme, CA 93043-4370

USA

Phone: (805) 982-1447; Fax: (805) 982-1074

luis.malvar@navy.mil

PRESENTED FOR THE
2007 FAA WORLDWIDE AIRPORT TECHNOLOGY TRANSFER CONFERENCE
Atlantic City, New Jersey, USA

April 2007

ABSTRACT

Recent concrete pavement failures due to alkali-silica reaction (ASR) point to the need to use supplementary cementitious materials, such as fly ash and ground granulated blast furnace slag to prevent deleterious expansions. Recent research has shown the effect of fly ash chemical composition on its effectiveness in mitigating ASR, and has allowed the determination of minimum cement replacement values to prevent deleterious expansions. Minimum replacement values are proposed for use even when the aggregate is labeled as innocuous. The potential impact of these observations on Department of Defense specifications is discussed.

INTRODUCTION

A state-of-the-art review [1,2] resulted in the development of guidelines to prevent alkali-silica reaction (ASR) now used by the Tri-Services (U.S. Navy, Air Force, and Army) for airfield pavements, and which are being adapted into Department of Defense (DOD) unified facilities guide specifications (UFGS) dealing with concrete in general. However, these guidelines are somewhat conservative for fly ash, allowing only the use of ASTM C 618 [3] Class F fly ashes with additional restrictions. Hence, many ashes very close to, but not meeting those specifications cannot be used, in some cases increasing concrete costs by requiring transportation of other ashes from far away. Recent research [4, 5] has shown that those specifications could be relaxed while insuring ASR mitigation. This paper presents a summary of the updated fly ash requirements and the proposed enhancements to the tri-service UFGS for concrete pavements.

BACKGROUND

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, strained quartz, cristobalite, etc. The products of this reaction often result in concrete expansion, cracking, and ultimately failure of the concrete structure, including significant potential for foreign object damage to aircraft. Alkali aggregate reaction (AAR) is the reaction between the cement hydroxides and mineral phases in the aggregates. In this paper no distinction is made between AAR and ASR. ASR needs several components to occur: alkali (supplied by the cement or external sources), water (or high moisture content or humidity), and a reactive aggregate.

There are 3 characteristics of a fly ash that determine its efficiency in preventing ASR:

- Fineness – Finer pozzolans are more efficient in reducing ASR expansion, e.g., Malhotra et al. [6] state: “fineness of fly ashes is one of the most important physical properties affecting pozzolanic activity” (see also Ravina [7], and Bérubé et al.[8]). Ultra fine fly ash (UFFA) [9], with particle sizes around 3 μm , is very effective, despite a CaO content around 11.8%. Raw silica fume, with particle sizes around 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, e.g., Mehta [10] showed the importance of mineralogy in mitigating sulfate attack.
- Chemistry – Previous models based only on chemistry have resulted in successful determination of the fly ash potential for ASR mitigation [4, 5, 11, 12].

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 generally be limited, and this factor will be 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 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 (e.g., α and β described below), 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 correlation [4, 5, 11, 12].

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 [13] (also called the accelerated mortar bar test, or 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 [14]). Fly ash and cement compositions for all five studies are shown in Tables 1 and 2, except for most of the Class C fly ashes, which can be found in Malvar and Lenke [4], together with the 14-day expansions of the cement alone, E_{14c} , and of the cement and fly ash blends, E_{14b} .

McKeen et al. [15, 16] tested 5 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 30317] (similar to ASTM C 1260 or CSA A23.2-25A [18]) was used to find the 14-day control expansions (E_{14c}). Shehata and Thomas [11] tested 18 ashes (with 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 (CSA) specifications [19] 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. [20, 21] evaluated a Type F ash ($\text{CaO} = 12.3\%$) and a Type C ash ($\text{CaO} = 26.1\%$) with 6 reactive aggregates and one Type I/II high-alkali cement (1.14% $\text{Na}_2\text{O}_{\text{eq}}$). Shon et al. [22] 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 sand with $E_{14c} = 0.245\%$. Detwiler [23] cites data using the 14-day AMBT with low, medium, and high CaO fly ashes (5.7%, 18.6%, 25.7%, respectively), a Type I low-alkali cement (0.43% $\text{Na}_2\text{O}_{\text{eq}}$), and 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, i.e., 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 mix with a blend of cement and fly ash, E_{14b} , was normalized by the expansion of the mix with cement only, E_{14c} . The chemical constituents are divided into two groups: those that increase expansion (CaO , Na_2O , K_2O , MgO , and SO_3) and those that reduce it (SiO_2 , Al_2O_3 , Fe_2O_3).

Table 1. Fly ash composition and chemical index, C_{fa} .

Fly Ash	Study ^a	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	MgO	Na ₂ O _{eq} ^b	ASTM	SUM	CSA	C_{fa} ^c
Winyah St.	^d	53.54	27.24	8.85	1.34	0.10	0.99	0.63	F	89.6	F	0.18
ENX	^d	67.40	20.20	4.59	5.29	0.02	1.00	1.36	F	92.2	F	0.26
Escalante(EF)	NM	61.34	25.11	4.42	4.94	0.08	1.09	1.25	F	90.9	F	0.27
4-Corners(4F)	NM	62.56	25.10	4.68	2.81	0.00	0.81	2.40	F	92.3	F	0.29
34-3	M&R ^d	35.50	12.50	44.70	1.89	0.75	0.63	1.25	F	92.7	F	0.29
87-156	M&R ^d	55.50	18.60	4.30	7.00	0.30	0.80	1.19	F	78.4	F/CI	0.31
34-4	M&R ^d	38.30	12.80	39.70	4.49	1.34	0.43	1.15	F	90.8	F	0.33
Coronado(CF)	NM	63.37	22.26	5.34	3.60	0.02	1.06	2.53	F	91.0	F	0.33
MN	S&T	61.50	20.52	4.29	8.68	0.19	1.70	0.56	F	86.3	F/CI	0.36
34-6	M&R ^d	48.00	21.50	10.60	6.72	0.52	0.96	1.13	F	80.1	F/CI	0.36
87-219	M&R ^d	62.00	20.10	2.00	6.90	0.60	1.20	1.49	F	84.1	F/CI	0.37
34-2	M&R ^d	44.10	21.40	26.80	1.95	0.96	0.99	2.09	F	92.3	F	0.38
34-5	M&R ^d	45.10	22.20	15.70	3.77	1.40	0.91	1.58	F	83.0	F	0.40
34-9	M&R ^d	62.10	21.40	2.99	11.00	0.16	1.76	0.77	F	86.5	CI	0.40
87-147	M&R ^d	57.90	26.30	3.90	9.60	0.40	2.10	0.26	F	88.1	F/CI	0.40
FM	S&T	47.34	22.34	15.08	6.38	1.43	0.82	1.41	F	84.8	F/CI	0.41
34-1	M&R ^d	47.10	23.00	20.40	1.21	0.67	1.17	2.62	F	90.5	F	0.41
34-8	M&R ^d	55.60	23.10	3.48	12.30	0.30	1.21	2.00	F	82.2	CI	0.49
LowCaO(DL)	Det.	44.80	23.54	16.98	5.66	1.22	1.26	2.07	F	85.3	F	0.50
LG	S&T	41.96	19.64	20.07	5.57	0.95	1.19	2.30	F	81.7	F	0.52
87-239	M&R ^d	48.90	18.50	21.80	7.30	0.50	2.60	0.99	F	89.2	F/CI	0.54
87-159	M&R ^d	57.50	20.60	7.00	9.10	0.20	2.60	1.32	F	85.1	F/CI	0.54
F-Ash (IF)	Touma	56.50	19.30	4.70	12.30	1.50	2.30	0.30	F	80.5	CI	0.57
UFFA ^e	^d	50.66	27.24	3.06	11.80	1.03	2.51	0.35	F	81.0	CI	0.57
87-154	M&R ^d	62.30	20.90	2.20	6.10	0.50	0.70	5.48	F	85.4	F/CI	0.58
87-157	M&R ^d	52.80	23.60	8.90	9.50	0.40	2.70	1.63	F	85.3	F/CI	0.61
87-155	M&R ^d	52.20	18.00	10.50	11.90	1.30	2.50	0.46	F	80.7	CI	0.61
SD II	S&T	51.56	22.90	4.58	15.15	0.28	1.16	2.80	F	79.0	CI	0.62
SD I	S&T	50.92	23.64	4.62	13.63	0.23	0.86	3.77	F	79.2	CI	0.63
34-7	M&R ^d	55.70	20.40	4.61	10.70	0.38	1.53	5.22	F	80.7	CI	0.77
Esc/Tolk(ET) ^f	NM	50.19	22.25	4.68	14.73	0.59	3.23	1.67	F	77.1	CI	0.82
87-146	M&R ^d	50.30	20.20	5.50	14.40	0.70	4.00	1.69	F	76.0	CI	0.93
86-805	M&R ^d	46.40	24.50	4.90	13.70	0.60	4.00	1.95	F	75.8	CI	0.96
BarbersPoint ^g	^d	43.47	18.42	6.30	15.72	6.56	1.45	1.40	^h	68.2	CI	1.11
CI	S&T	44.29	20.96	5.23	17.51	2.13	4.21	1.68	F	70.5	CI	1.21
85-147	M&R ^d	50.40	21.40	3.50	11.60	0.50	3.00	7.19	F	75.3	CI	1.21
87-144	M&R ^d	47.90	21.90	4.90	13.30	1.10	2.90	6.76	F	74.7	CI	1.26
MedCaO(DM)	Det.	41.00	21.50	6.03	18.62	1.10	4.62	2.25	C	68.5	CI/CH	1.32
BD II	S&T	45.66	21.42	5.53	12.34	0.84	2.76	8.45	F	72.6	CI	1.40
34-10	M&R ^d	46.30	22.10	3.10	13.30	0.80	3.11	7.81	F	71.5	CI	1.41
83-275	M&R ^d	45.60	15.50	7.30	20.30	1.90	5.00	2.12	C	68.4	CI/CH	1.42

^a S&T: Shehata&Thomas¹¹; NM: McKeen.¹⁵; Det: Detwiler²³; Touma²¹; Shon²²; M&R: Malhotra⁶.

^b Total alkalis

$$C_{fa}^c = \frac{CaO_{eq\alpha fa}}{SiO_{2eq\beta fa}} = \frac{CaO + 6.0(0.905Na_2O + 0.595K_2O + 1.391MgO + 0.700SO_3)}{SiO_2 + 1.0(0.589Al_2O_3 + 0.376Fe_2O_3)}$$

^d These ashes were not used in model development but in demonstrating model usage.

^e Ultra fine fly ash (UFFA) composition provided by Boral Material Technologies.

^f 50/50 blend of two ashes: Escalante Type F and Tolk Type C.

^g Barber's Point fly ash composition provided by Hawaiian Cement.

^h Meets neither C nor F fly ash specifications.

Table 2.
Portland cement composition and chemical index, C_c .

Cement Type	Study ^a	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	MgO	Na ₂ O _{eq}	C_c ^b
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
Med Alkali	Shon	19.12	5.07	3.40	64.73	3.13	0.64	0.65	3.71

^a S&T: Shehata and Thomas¹¹; NM: McKeen, et al.¹⁵; Detwiler²³; Touma²¹; Shon²².

$$C_c = \frac{CaO_{eqac}}{SiO_{2eq\beta c}} = \frac{CaO + 6.0(0.905Na_2O + 0.595K_2O + 1.391MgO + 0.700SO_3)}{SiO_2 + 1.0(0.589Al_2O_3 + 0.376Fe_2O_3)}$$

Calcium Oxide (CaO)

The fly ash content of calcium oxide (or lime) has been shown to have the most effect on the efficiency of the ash in mitigating ASR [1, 11, 15]. Current DOD guidelines for pavements do not allow Class C fly ash and limit the CaO content of Class F fly ash to 8% based on the original research [1]. The New Mexico State Highway and Transportation Department [24] now places an 8% restriction as well. Canadian guidelines even classify fly ashes based on CaO content [19] and use the same 8% CaO limit for Class F. A good correlation was found between the normalized expansion and the CaO content of the blend with a coefficient of determination $R^2 = 0.71$ (Figure 1). The CaO content varied from about 3 to 30% for the ashes, and from about 63 to 65% for the cements (Tables 1, 2). Since the cement CaO content was fairly constant, the total cementitious (cement plus fly ash) CaO variation is mostly due to the ash CaO content.

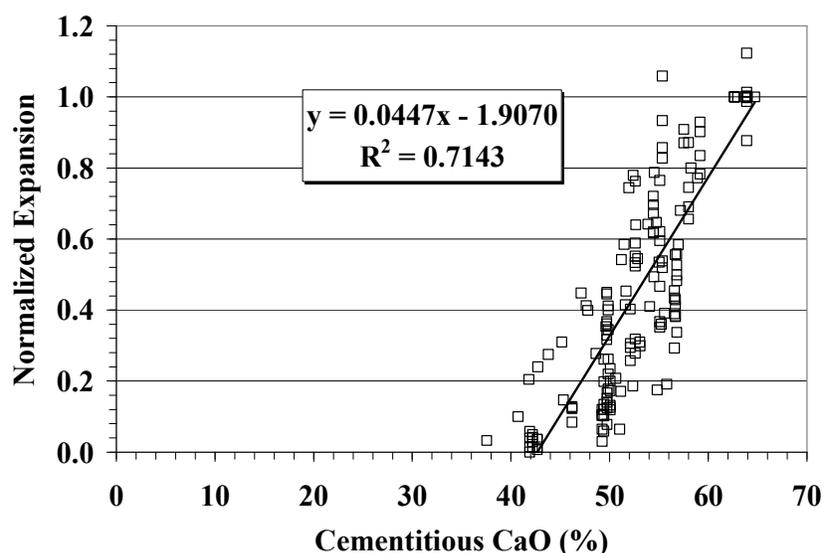


Figure 1. Effect of total CaO content (in cement and fly ash) on 14-day AMBT expansion.

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 ($\leq 0.6\%$ total alkali), and for fly ash, either the total or the available alkalis are often limited. However, mixes with low-alkali cement and ashes, and with large variation in the other constituents, 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 mix (as indicated under Significance and Use). Thomas and Shehata [12] found a good correlation between $\text{CaO}/(\text{SiO}_2)^2$ 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 [3] no longer includes the 1.5% available alkali limit as a supplementary optional chemical requirement. However, since reactive aggregates are very sensitive to alkali and the cement alkali is limited, it seems that some limit on fly ash alkalis should be maintained.

Several specifications recognize that the alkali in the fly ash should be limited, but there is no consensus on the optimum limit. Some specifications limit [24], or used to limit [3] the available alkalis to 1.5%. Other specifications recommend limiting the total alkali in the concrete mix, accounting for either none of the fly ash alkali (if enough fly ash is used to prevent ASR, e.g. 25% replacement), or a percentage of it (20 to 100%) [25, 26, 27, 28], indirectly limiting the fly ash alkalis. Finally, some specifications have limited the total fly ash alkalis, for example to 2% [29], 3% [28], and 5% [30]. It is proposed to limit the total alkalis to 3% instead of limiting the available alkalis – this would allow for simple alkali control, while affecting few fly ashes (less than 20% of those in Table 1).

Magnesium Oxide (MgO)

AASHTO M 295 [31] (similar to ASTM C 618) used to require a 5% MgO limit in the fly ash to prevent deleterious expansion from the formation of magnesium hydroxide. This limit is still enforced, for example, by the New Mexico State Highway and Transportation Department [24]. Class F fly ashes typically have very little MgO, but Class C ashes are likely to have more [6]. However, Mehta [32] 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. For the current data, a very weak correlation between normalized expansion and MgO content was indeed found [5], with $R^2 = 0.05$.

Sulfur Trioxide (SO₃)

Sulfur trioxide is limited to a maximum of 5% in ASTM C 618 for both Class C and F ashes, and has previously been found to increase deleterious expansion [1]. Figure 2 shows a moderate correlation ($R^2 = 0.50$) between normalized expansion and cementitious SO₃ content.

Silicon Dioxide (SiO₂)

Silicon dioxide shows pozzolanic activity, i.e., forms a cementitious product by reaction with calcium hydroxide. Increased contents of SiO₂ have shown to lower ASR expansion. Figure 3 shows a significant inverse correlation ($R^2 = 0.74$) between the cementitious SiO₂ content and the normalized 14-day expansion.

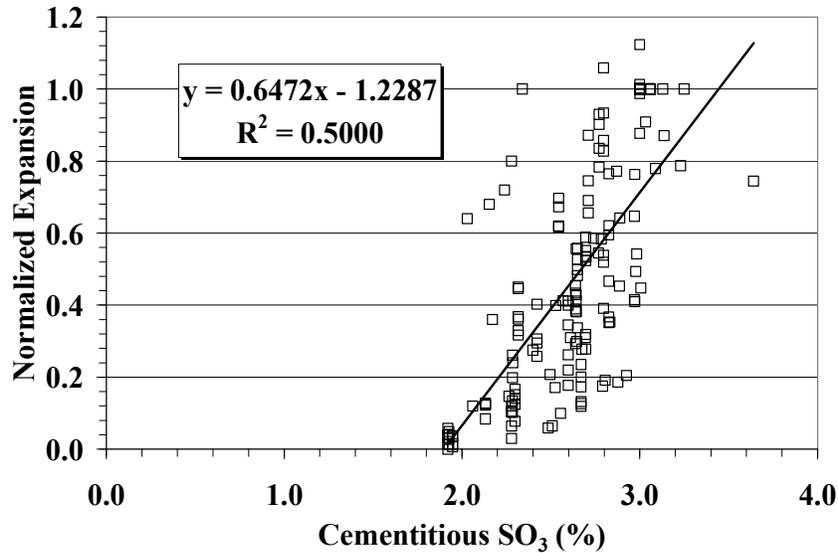


Figure 2. Effect of total SO_3 content (in cement and fly ash) on 14-day AMBT expansion.

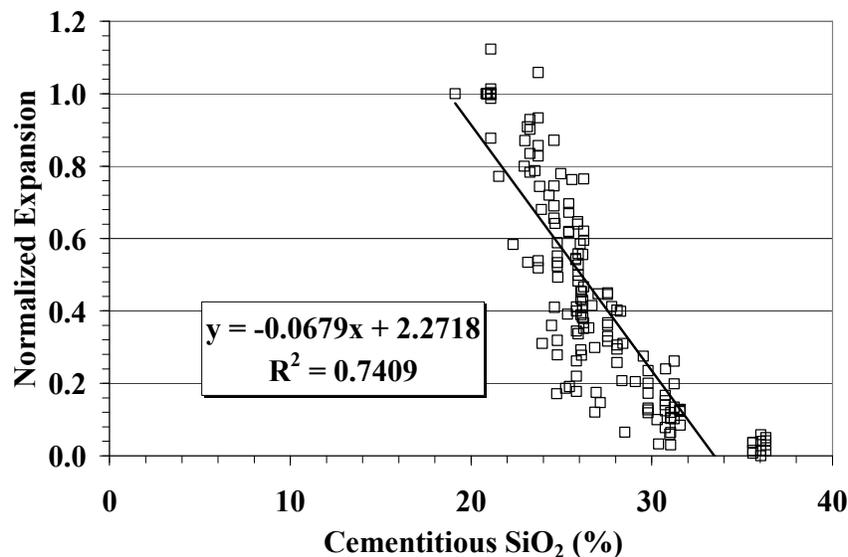


Figure 3. Effect of total SiO_2 content (in cement and fly ash) on 14-day AMBT expansion

Aluminum Trioxide (Al_2O_3)

Alumina can contribute to the pozzolanic effect of silica, and often the sum $\text{SiO}_2 + \text{Al}_2\text{O}_3$ has shown good correlation with pozzolanic activity [6]. Figure 4 shows the inverse correlation ($R^2 = 0.60$) between normalized expansion and cementitious Al_2O_3 content.

Iron Oxide (Fe_2O_3)

Malhotra et al. [6] report that for most ashes the iron oxide is present as nonreactive hematite and magnetite, so a weak correlation would be expected. For the present data, a weak inverse correlation ($R^2 = 0.13$) between expansion and cementitious Fe_2O_3 content was indeed found [1].

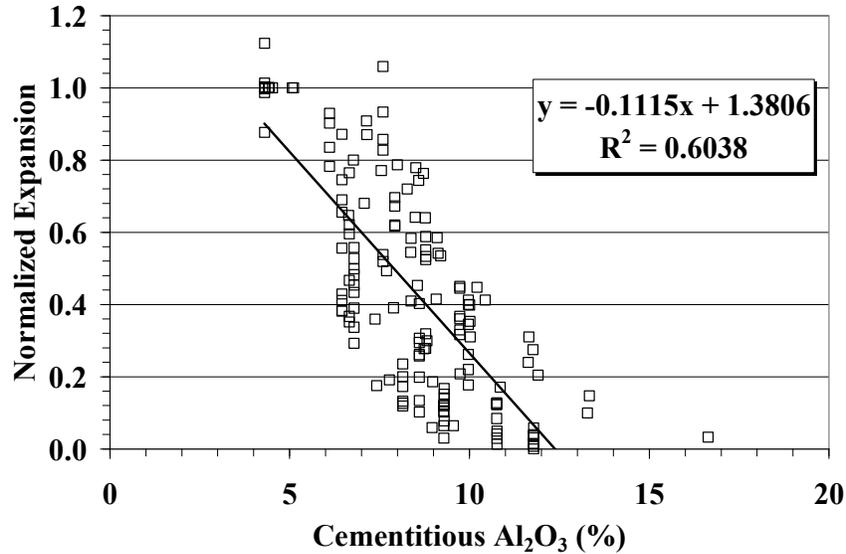


Figure 4. Effect of total Al_2O_3 content (in cement and fly ash) on 14-day AMBT expansion

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:

$$\text{CaO}_{\text{eq}} = \text{CaO} + 0.905 \text{Na}_2\text{O}_{\text{eq}} + 1.391 \text{MgO} + 0.700 \text{SO}_3 \quad (1)$$

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

$$\text{CaO}_{\text{eq}} = \text{CaO} + 0.905 \text{Na}_2\text{O} + 0.595 \text{K}_2\text{O} + 1.391 \text{MgO} + 0.700 \text{SO}_3 \quad (2)$$

The correlation between normalized 14-day expansion and cementitious CaO_{eq} ($R^2 = 0.78$) is better than any previous correlation with a single constituent promoting expansion (Figures 1 and 2) or other combinations thereof [45].

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:

$$\text{SiO}_{2\text{eq}} = \text{SiO}_2 + 0.589 \text{Al}_2\text{O}_3 + 0.376 \text{Fe}_2\text{O}_3 \quad (3)$$

A strong inverse correlation ($R^2 = 0.78$) was found between expansion and cementitious $\text{SiO}_{2\text{eq}}$, better than any previous correlation with a single component reducing expansion (Figures 3 and 4) or other combinations thereof [45].

Combination of All Constituents

The normalized expansion was correlated to the ratio $\text{CaO}_{\text{eq}}/\text{SiO}_{2\text{eq}}$ (using equations 1 and 3, or 2 and 3), resulting in a correlation $R^2 = 0.83$, which is an improvement from the correlations with just CaO_{eq} or $\text{SiO}_{2\text{eq}}$. 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 to this data is trilinear, with two segments of zero slope at low and high replacement levels (as proposed by Thomas and Shehata [12]) resulting in a correlation $R^2 = 0.867$ (Figure 5).

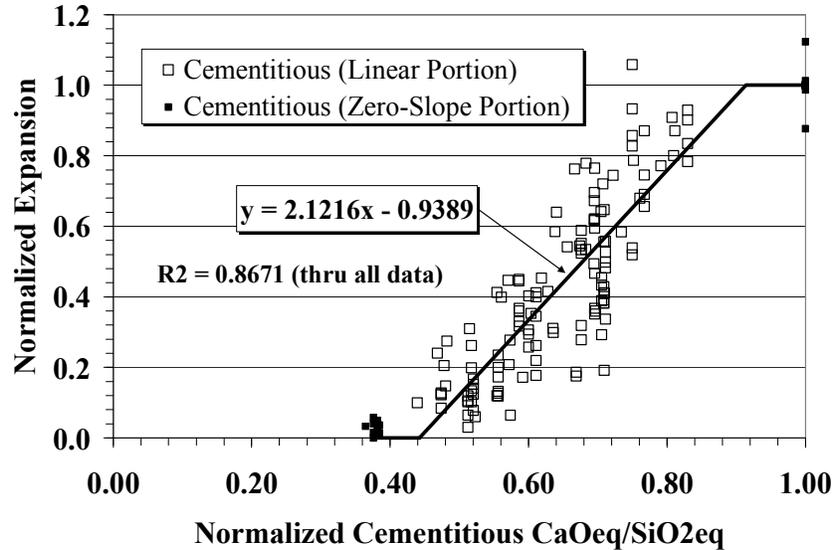


Figure 5. Effect of normalized $\text{CaO}_{\text{eq}}/\text{SiO}_{2\text{eq}}$ ratio on 14-day AMBT expansion.

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 SiO_2 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 :

$$C_b = \frac{\text{CaO}_{\text{eq}\alpha\beta}}{\text{SiO}_{2\text{eq}\beta}} = \frac{\text{CaO} + \alpha(0.905\text{Na}_2\text{O} + 0.595\text{K}_2\text{O} + 1.391\text{MgO} + 0.700\text{SO}_3)}{\text{SiO}_2 + \beta(0.589\text{Al}_2\text{O}_3 + 0.376\text{Fe}_2\text{O}_3)} \quad (4)$$

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 Figure 5 is obtained [4] 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 constituent. The same chemical index can be defined for a blend with only cement (0% ash), denoted C_c , and for a blend with only fly ash (100% ash), denoted C_{fa} .

Finally, the best fit is obtained using a non-linear hyperbolic tangent model [5] as follows:

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

where $\alpha = 4.42$, $\beta = 0.754$, $a_1 = 1.0550$, $a_2 = 0.7342$, $a_3 = 0.1834$, and $R^2 = 0.9149$. The value of R^2 does not change significantly for values of α and β near the previous ones, and for simplicity $\alpha = 6$ and $\beta = 1$ were adopted, with $a_1 = 1.0530$, $a_2 = 0.7386$, $a_3 = 0.1778$, yielding $R^2 = 0.9125$, as shown by the solid line in Figure 6. 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 (Table 1), cement (Table 2), and blends, 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.

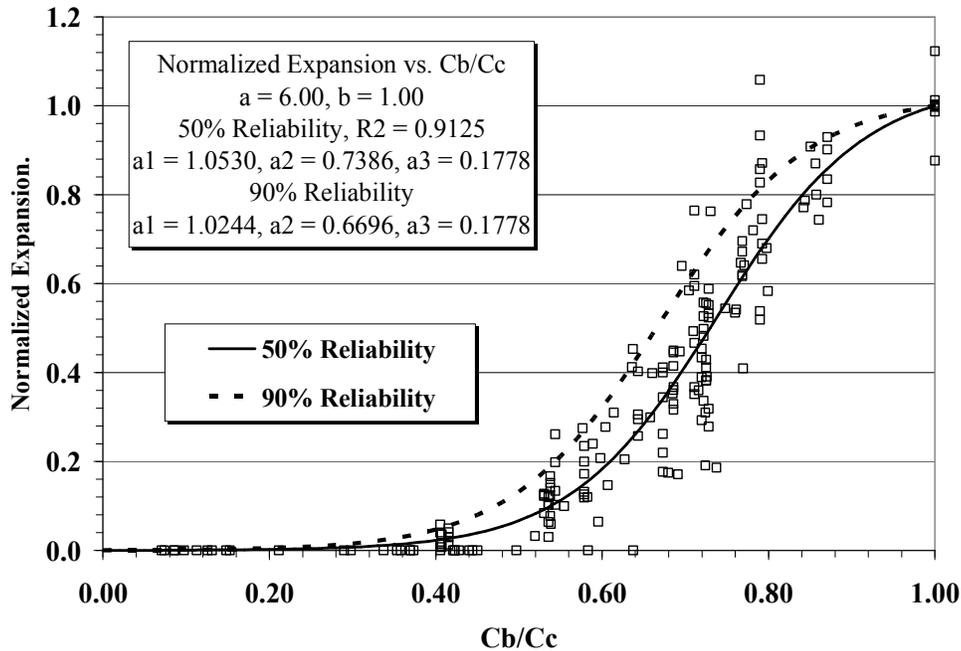


Figure 6. Effect of C_b/C_c ratio on AMBT expansion (hyperbolic tangent model).

Fly Ash Chemical Index

Table 1 ranks all the ashes studied by increasing chemical index, C_{fa} . It is seen that a value of $C_{fa} < 1.4$ usually represents an ASTM C 618 Class F ash, and values $C_{fa} > 1.4$ usually represent a Class C ash. When compared to the Canadian standard (CSA A3001, 2003), a value of $C_{fa} < 0.5$ usually represents a Canadian Class F ash, $0.5 < C_{fa} < 1.4$ usually represents a Class CI ash, and values $C_{fa} > 1.4$ 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 mix to be non-reactive. This can be accomplished starting from Figure 6. The maximum ASTM C 1260 14-day expansion sought is 0.08% [1], and if E_{14c} is the AMBT expansion with cement only, then the maximum normalized expansion sought in Figure 6 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 Figure 6 as function “g” it can be shown [5] that the minimum required percent fly ash substitution by weight, W , is:

$$W = \frac{1 - g(0.08 / E_{14c})}{\left(1 - \frac{CaO_{eq\alpha fa}}{CaO_{eq\alpha c}}\right) - \left(1 - \frac{SiO_{2eq\beta fa}}{SiO_{2eq\beta c}}\right) g(0.08 / E_{14c})} \quad (6)$$

This formula gives the minimum required fly ash substitution as a function of three sets of inputs: the ash chemistry (given by $CaO_{eq\alpha fa}$ and $SiO_{2eq\beta fa}$), the cement chemistry (given by $CaO_{eq\alpha c}$ and $SiO_{2eq\beta c}$), and the 14-day AMBT expansion with cement only (E_{14c}). 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 Figure 7 for a cement with chemical index $C_c = 4.0$. In this figure, the first 4 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 used in model development). 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. The least effective Class C ashes ($C_{fa} \approx 2.65$) could only mitigate very low reactivity aggregates for typical replacement amounts.

The minimum replacement from Figure 7 is based on using the best fit to the data in Figure 6 (i.e., a 50% reliability level). For design, it is recommended to use a 90% reliability level, represented by the dashed curve in Figure 6 (with $a_1 = 1.0244$, $a_2 = 0.6696$ and $a_3 = 0.1778$). 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, Figure 8 is obtained, which gives the minimum required replacement with a reliability of 90% that the expansion will be less than the stipulated 0.08%. Figures 7 and 8 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, these figures could be used as an approximation to find the minimum replacement for typical cements.

CLASSIFICATION USING THE CHEMICAL INDEX

As indicated earlier, the fly ash chemical index C_{fa} has a good correlation with ASTM C 618. Table 1 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. When compared to the Canadian standard [19], the chemical index also shows good agreement, with a few exceptions. For example, ash MN is a CI ($CaO > 8\%$) but appears within the CSA Type F ashes: this ash has an ASTM sum $SiO_2 + Al_2O_3 + Fe_2O_3 = 86.3\%$ 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, since 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”). Similarly, many other ashes using the CSA classification appear out of order when compared to the C_{fa} or ASTM ranking for ASR mitigation effectiveness (see also Malvar and Lenke [5] for ranking of Class CI and CH ashes). Hence this CSA classification is not recommended.

As an additional comparison, the ASTM sum ($SiO_2 + Al_2O_3 + Fe_2O_3$) is also shown in Table 1 (under SUM). 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.

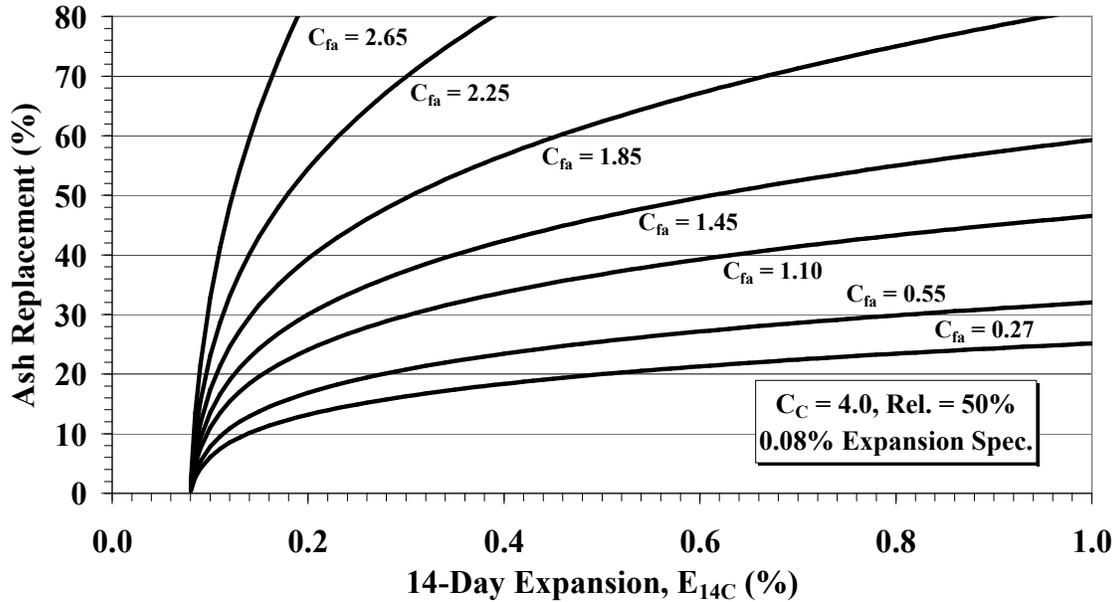


Figure 7. Minimum fly ash replacement to mitigate ASR with 50% reliability

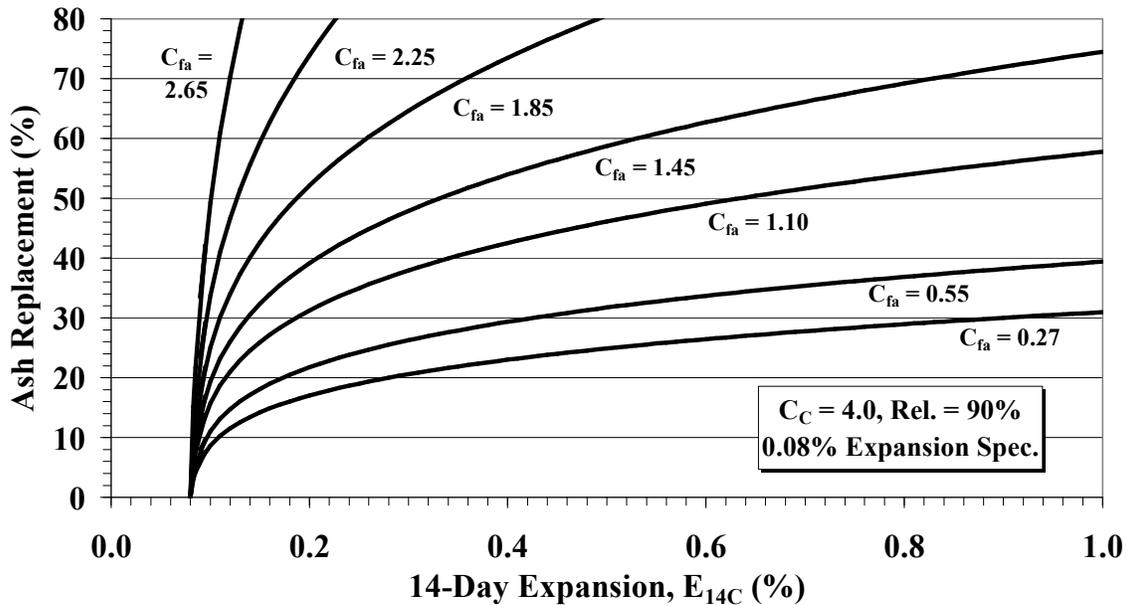


Figure 8. Minimum fly ash replacement to mitigate ASR with 90% reliability.

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. For this fly ash the chemical index is 1.11, making it equivalent to an ASTM C 618 Class F ash in Table 3. Another interesting ash is an UFFA9], also shown in Table 1. While the most important

characteristic of UFFA is its fineness, its chemical composition includes 11.8% CaO, 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 (see Table 1), in addition to the benefits of its fineness.

APPLICATION TO GUIDE SPECIFICATIONS

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 also use absolute minimum replacements depending on the application, whether or not the aggregates are reactive, since the resulting concrete will, in general, be cheaper and more durable. For example, the U.S. Navy currently requires a minimum of 25% Class F fly ash (with $\text{CaO} \leq 8\%$ and available alkalis $\leq 1.5\%$) in pavements independently of reactivity [1], and the New Mexico State Highway and Transportation Department [24] requires 20% Class F minimum (with the same limits on CaO and available alkalis, and with $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 85\%$, or Class C if the aggregate is innocuous).

Current DOD specifications for Class F ash ($\text{CaO} \leq 8\%$ and available alkalis $\leq 1.5\%$) limit the ashes usable to about the top 40% of those shown in Table 1, and correspond approximately to requiring a sum $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 80$ to 85%. If the requirements are relaxed to $\text{CaO} \leq 13\%$ and total alkalis $\leq 3\%$, then approximately the top two-thirds of the Class F ashes in Table 1 could be used (this corresponds approximately to requiring a sum $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 80\%$). These are the proposed fly ash requirements for the UFGS update to address reactive aggregates (together with a maximum allowable expansion of 0.08% per ASTM C 1567 for the final mix).

For non-reactive aggregates, the Navy currently requires a minimum of 25% Class F ash with $\text{CaO} \leq 8\%$ and available alkalis $\leq 1.5\%$. If the aggregates are innocuous (expansion $< 0.08\%$), these are severe restrictions on the ash, since a 25% cementitious content of such ashes can mitigate up to 0.45% reactivity (see Figure 9 for 50% reliability) and this is not needed. Instead, for non-reactive aggregates, it is proposed to (1) remove the CaO limit, (2) require total alkalis $\leq 3\%$, and (3) require the following minimum fly ash contents:

- 25% if $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 70\%$
- 20% if $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 80\%$
- 15% if $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 90\%$

It can be seen from Figure 9 that these minimum replacements could mitigate a reactivity of about 0.2% or more, providing some safety since the actual reactivity is 0.08% or less in this case. For innocuous aggregates, Figure 9 also shows that using a 30% content of a Class C ash with $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 65\%$ would also provide a similar benefit (there are 2 such ashes at the bottom of Table 1). For DOD applications, the use of such Class C ashes could be possible but would have to be addressed on a case by case basis.

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 in particular 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 insure with 90% reliability that the 14-day AMBT expansion would remain below 0.08%.

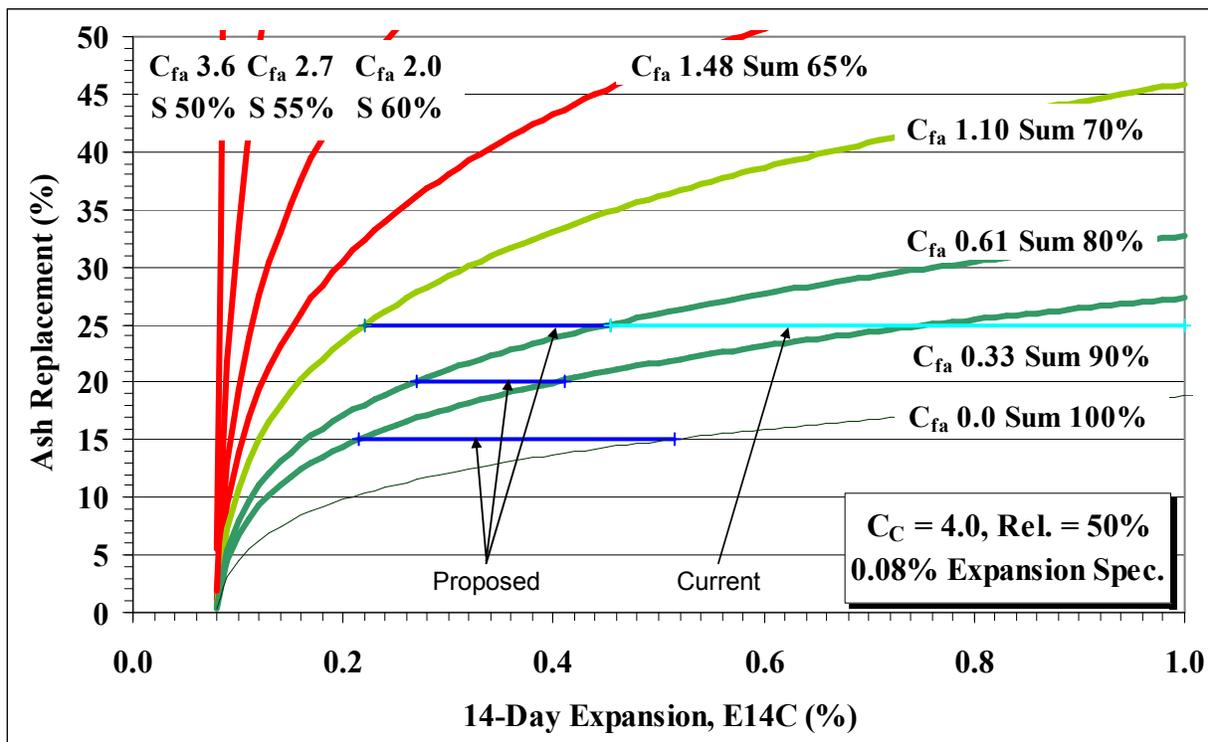


Figure 9. Determination of minimum fly ash replacement requirements.

It is proposed that current guidelines for fly ash for use in DOD airfield concrete pavements be modified as follows:

- For non-reactive aggregates, use Class F fly ash with total alkalis $\leq 3\%$, and require the following minimum fly ash contents:
 - 25% if $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 70\%$
 - 20% if $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 80\%$
 - 15% if $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 90\%$
- For reactive aggregates, use Class F fly ash with the additional requirements of $\text{CaO} \leq 13\%$ and total alkalis $\leq 3\%$ (together with a maximum allowable expansion of 0.08% per ASTM C 1567 for the final mix). Required replacements to mitigate reactivity can be estimated with Figure 9, and should exceed the minimum requirements for non-reactive aggregates.

ACKNOWLEDGMENTS

This work was supported by the Naval Facilities Engineering Command mission funding for the Pavement Design Technical Center of Expertise.

REFERENCES

1. Malvar, L.J., Cline, G.D., Burke, D.F., Rollings, R., Sherman, T.W., Greene, J., "Alkali Silica Reaction Mitigation: State-of-the-Art and Recommendations," *ACI Materials Journal*, Vol. 99, No. 5, pp. 480-489, 2002.
2. Malvar, L.J., Cline, G.D., Burke, D.F., Rollings, R., Sherman, T.W., Greene, J., Closure to the Discussion of "Alkali Silica Reaction Mitigation: State-of-the-Art and Recommendations," *ACI Materials Journal*, Vol. 100, No. 4, pp. 346-350, 2003.
3. ASTM C 618, "Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Concrete," American Society for Testing and Materials, 2003.
4. Malvar, L.J., Lenke, L.R., "Minimum Fly Ash Cement Replacement to Mitigate Alkali Silica Reaction," *Proceedings, World of Coal Ash (WOCA 2005)*, Lexington, KY, 2005, <http://www.flyash.info/2005/170mal.pdf>
5. Malvar, L.J., Lenke, L.R., "Efficiency of Fly Ash in Mitigating Alkali Silica Reaction Based on Chemical Composition," *ACI Materials Journal*, Vol. 103, No. 5, pp. 319-326, September-October 2006.
6. Malhotra, V.M., Ramezaniapour, A.A., "Fly Ash in Concrete," MSL 94-45(IR), CANMET, Canada Center for Mineral and Energy Technology, Natural Resources Canada, Ottawa, Ontario, Canada, 307 pp., 1994.
7. Ravina, D. (1980), "Optimized Determination of PFA (fly ash) fineness with reference to pozzolanic activity," *Cement and Concrete Research*, Vol. 10, pp. 573-580.
8. Bérubé, M.A., Carles, A., Duchesne, J., Naproux, P., "Influence of Particle Size Distribution on the Effectiveness of Type-F Fly Ash in Suppressing Expansion Due to Alkali-Silica Reactivity" 5th CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Milwaukee, USA, ACI SP-153, pp. 177-192, 1995.
9. Obla, K.H., Hill, R.L., Thomas, M.D.A., Shashiprakash, S.G., Perebatova, O. (2003), "Properties of Concrete Containing Ultra Fine Fly Ash," *ACI Materials Journal*, Vol. 100, No. 5, pp. 426-433.
10. Mehta, P.K., "Effect of Fly Ash Composition on Sulfate Resistance of Cement," *ACI Journal*, Vol. 83, No. 6, November/December, pages 994-1000, 1986.
11. Shehata, M.H., Thomas, M.D., "The Effect of Fly Ash Composition on the Expansion of Concrete due to Alkali Silica Reaction," *Cement & Concrete Research*, Vol. 30, pp. 1063-1072, 2000.
12. Thomas, M.D.A., Shehata, M.H., "Use of Blended Cements to Control Expansion of Concrete due to Alkali Silica Reaction," 8th CANMET/ACI International Conference on Fly ash, Silica Fume, Slag, and Natural Pozzolans, Supplementary Papers, Las Vegas, NV, pp. 591-607, 2004.
13. ASTM C 1260, "Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)," American Society for Testing and Materials, 2003.

14. ASTM C 1567, "Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)," American Society for Testing and Materials, 2004.
15. McKeen, R.G., Lenke, L.R., Pallachulla, K.K., "Mitigation of Alkali-Silica Reactivity in New Mexico," Report to the Research Bureau, New Mexico Department of Transportation, by ATR Institute, Materials Research Center, University of New Mexico, Albuquerque, NM, 23 pp., 1998.
16. McKeen, R.G., Lenke, L.R., Pallachulla, K.K., Barringer, W.L., "Mitigation of Alkali-Silica Reactivity in New Mexico," Transportation Research Record, No. 1698, pp. 9-16, 2000.
17. AASHTO T 303, "Accelerated Detection of Potentially Deleterious Expansion of Mortar Bars Due to Alkali-Silica Reaction," Standard Specifications for Transportation Materials and Methods of Sampling and Testing: Part II – Tests, American Association of State Highway and Transportation Officials, 4 pp., 2000.
18. CSA A23.2-25A, "Test Method for Detection of Alkali Silica Reactive Aggregate by Accelerated Expansion of Mortar Bars," Canadian Standards Association, Toronto, Ontario, CA, 5 pp., 2000.
19. CSA A3001, "Cementitious Materials for Use in Concrete," Canadian Standards Association, CSA International, Toronto, Ontario, CA, 30 pp., 2003.
20. Touma, W.E., Suh, C., Fowler, D.W., Carrasquillo, R.L., Folliard, K.J., "Alkali Silica Reaction in Portland Cement Concrete: Testing Procedures and Mitigation Methods," 11th Intl. Conference on Alkali Aggregate Reaction, Québec City, Canada, pp. 513-522, 2000.
21. Touma, W.E., Fowler, D.W., Carrasquillo, R.L., "Alkali Silica Reaction in Portland Cement Concrete: Testing Methods and Mitigation Alternatives," Research Report ICAR 301-1F, International Center for Aggregates Research, 520 pp., 2001.
22. Shon, C.-S., Zollinger, D. G., Sarkar, S. L., "Evaluation of ASR Resistance of Fly Ash-Slag Combinations Using the Modified ASTM C 1260 Test Method," 8th CANMET/ACI Intl. Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, SP-221, V.M. Malhotra, ed., American Concrete Institute, Farmington Hills, MI, pp. 249-264, 2004.
23. Detwiler, R.J., "PCA's Guide Specification for Concrete Subjected to Alkali-Silica Reactions: Mitigation Measures," R&D Serial 2407, Portland Cement Association, Skokie, IL, 11 pp., 2003.
24. New Mexico State Highway and Transportation Department, Interim Specifications for Portland Cement Concrete, Section 510, Standard Specifications for Highway and Bridge Construction, State Construction Bureau, Santa Fe, NM, 2005.
25. Cement and Concrete Association of New Zealand, "Alkali Silica Reaction - Minimising the Risk of Damage to Concrete Guidance Notes and Recommended Practice," TR3 (Second Edition), 2003 (<http://www.cca.org.nz/shop/downloads/TR03.pdf>).
26. Concrete Society, "Alkali Silica Reaction: Minimising the Risk of Damage to Concrete: Guidance Notes and Model Clauses for Specifications (3rd ed.)," Concrete Society Technical Report no. 30, United Kingdom, 1999.
27. Building Research Establishment, "Alkali-Silica Reaction in Concrete – Detailed Guidance for New Construction," BRE Digest 330 Part 2, 1999.
28. Cement and Concrete Association of Australia & Standards Australia, "Alkali Aggregate Reaction: Guidelines on Minimising the Risk of Damage to Concrete Structures in Australia," CCAA Technical Report: T47 (SAA HB79-1996), 1996.

29. Queensland Department of Main Roads (1999), "Main Roads Standard Specification – Concrete," MRS11.70, Queensland, Brisbane, Australia.
30. Building Research Establishment, "Alkali-silica reaction in concrete - Simplified Guidance for New Construction using Normal Reactivity Aggregates," BRE Digest 330 Part 4, 1999.
31. AASHTO M 295, "Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Concrete," Standard Specifications for Transportation Materials and Methods of Sampling and Testing: Part I – Specifications, American Association of State Highway and Transportation Officials, 3 pp., 2000.
32. Mehta, P.K., "Standard Specifications for Mineral Admixtures – An Overview," 2nd CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Madrid, Spain, ACI SP-91, pp. 637-658, 1986.