



Use of ternary blends containing silica fume and fly ash to suppress expansion due to alkali–silica reaction in concrete

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Abstract

This paper investigates the effects of cementitious systems containing Portland cement (PC), silica fume (SF) and fly ash (FA) on the expansion due to alkali–silica reaction (ASR). Concrete prisms were prepared and tested in accordance with the Canadian Standards Association (CSA A23.2-14A). Paste samples were cast using the same or similar cementitious materials and proportions that were used in the concrete prism test. Pore solution chemistry and portlandite content of the paste samples are reported. It was found that practical levels of SF with low-, moderate- or high-calcium FA are effective in maintaining the expansion below 0.04% after 2 years. Pore solution chemistry shows that while pastes containing SF yield pore solutions of increasing alkalinity at ages beyond 28 days, pastes containing ternary blends maintain the low alkalinity of the pore solution throughout the testing period (3 years). © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Alkali–aggregate reaction; Expansion; Pore solution; Fly ash; Silica fume

1. Introduction

The use of pozzolans or slag to control the expansion due to alkali–silica reaction (ASR) is well established and a number of reviews have been published recently [1–5]. In addition to numerous laboratory studies, the addition of moderate levels (e.g., 20–30%) of low-calcium Type F fly ash, in controlling ASR has been adequately demonstrated by long-term field performance [6]. FA with higher levels of calcium have been shown to be less efficacious in this role, with levels of replacement in excess of 50% being required with some FA when used in combination with highly reactive aggregate and high-alkali cement (HAPC) [3]. Under similar testing conditions, other workers [7] have shown that silica fume (SF) must be used at replacement levels exceeding 10% by mass of cementing materials. Replacement levels in excess of 50% FA or 10% SF may not be acceptable for many construction purposes and this presents a barrier to the wider use of these materials for controlling ASR.

This paper evaluates the performance of combinations of SF and FA for controlling ASR. FA of low, moderate and high calcium content, meeting the Canadian Standards Association (CSA A23.5) classification for Types F, CI and CH FA were included in the study. The efficiency of various blends of SF and FA was established using the concrete prism test. In addition, the evolution of the pore solution chemistry was established by expressing and analysing the solution from pastes at various ages up to 3 years.

2. Experimental methods

2.1. Materials

The materials used in this study were two HAPCs and one low-alkali Portland cements (LAPC) (1.00%, 1.09% and 0.60% Na₂O_e, respectively), a single source of high-silica, low-alkali SF and three FA of low, moderate and high calcium contents. The chemical compositions of the cementitious materials are given in Table 1. Note that the moderate-calcium FA (WM) has a relatively high alkali content (4.14% Na₂O_e). A siliceous limestone reactive coarse aggre-

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Table 1
Chemical composition of the ordinary Portland cement and pozzolans (mass%)

Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	Na ₂ O _e ^a	TiO ₂	P ₂ O ₅	AA ^b	LOI
<i>Portland Cement (PC)</i>													
HAPC 1	18.66	6.56	3.02	61.40	2.93	4.39	1.03	0.41	1.09	0.24	0.13	–	0.92
HAPC 2	20.83	5.11	2.01	62.98	2.43	3.25	1.12	0.28	1.00	0.24	0.05	–	0.92
LAPC	21.27	4.22	2.98	62.71	2.13	2.82	0.77	0.10	0.60	0.18	0.11	–	2.40
<i>Silica Fume (SF)</i>													
SF	96.94	0.52	0.14	0.58	0.00	0.13	0.42	0.04	0.31	0.01	0.09	–	1.47
<i>Fly Ash (FA)</i>													
FM	47.34	22.34	15.08	6.38	0.82	1.43	1.23	0.60	1.41	1.10	0.32	0.47	2.73
WM	39.77	21.46	5.69	18.46	3.77	1.86	0.66	3.71	4.14	1.04	0.54	2.52	1.06
OK	34.60	16.45	7.13	27.71	5.89	2.71	0.21	1.51	1.65	1.30	0.71	1.23	0.28

^a Acid-soluble alkali.

^b Available alkali, expressed as Na₂O_e, as per ASTM C 311.

gate from Ottawa (Spratt) and a nonreactive limestone crushed sand were used in the expansion testing.

2.2. Expansion testing

Concrete prisms were cast and tested in accordance with the Standard Concrete Prism Test (CSA A23.2-14A) using 420 kg/m³ of cementing materials and a water-to-cementing material ratio (W/CM) of 0.45. This test is essentially the same as ASTM C 1293. One control sample was cast with an alkali content of 5.25 kg/m³ Na₂O_e representing concrete made with PC of 1.25% Na₂O_e. Three other

control samples were prepared with Na₂O_e contents of 4.20, 3.70 and 3.15 kg/m³ of concrete. These three samples represent concrete, made with a PC of 1.25% Na₂O_e, in which 20%, 30% and 40%, respectively, of the PC contents were replaced by inert diluents. For the samples containing pozzolans (FA and SF), the Na₂O_e contents were adjusted to be 1.25% of the mass of PC. The alkali contents of the control samples (other than that with an alkali content of 5.25 kg/m³ Na₂O_e) were adjusted by mixing the LAPC and HAPC 2. The alkali contents of the control sample cast with an alkali content of 5.25 kg/m³ Na₂O_e and the samples containing pozzolans were adjusted by adding

Table 2
Sample combinations (mass%) and expansion (%) of concrete prisms at 2 years

Mix	SF (%)	FA (%)			Source of alkalis	Alkali content ^a Na ₂ O _e (kg/m ³)	Expansion at 2 years (%)
		FM	WM	OK			
PC 1	–	–	–	–	HAPC 2 + NaOH ^b	5.25	0.250
PC 2	–	–	–	–	HAPC 2	4.20	0.241
PC 3	–	–	–	–	HAPC 2 + LAPC ^c	3.70	0.164
PC 4	–	–	–	–	HAPC 2 + LAPC ^c	3.15	0.114
PC 5	–	–	–	–	HAPC 2 + LAPC ^c	2.89	0.044
15 FM	–	15	–	–	HAPC 2 + NaOH ^b	4.46	0.083
20 FM	–	20	–	–	HAPC 2 + NaOH ^b	4.20	0.043
30 WM	–	–	30	–	HAPC 2 + NaOH ^b	3.68	0.100
40 WM	–	–	40	–	HAPC 2 + NaOH ^b	3.15	0.068
50 WM	–	–	50	–	HAPC 2 + NaOH ^b	2.63	0.042
30 OK	–	–	–	30	HAPC 2 + NaOH ^b	3.68	0.138
45 OK	–	–	–	45	HAPC 2 + NaOH ^b	2.90	0.054
60 OK	–	–	–	60	HAPC 2 + NaOH ^b	2.10	0.021
5 SF	5	–	–	–	HAPC 2 + NaOH ^b	4.99	0.216
5 SF/10 FM	5	10	–	–	HAPC 2 + NaOH ^b	4.46	0.041
5 SF/15 FM	5	15	–	–	HAPC 2 + NaOH ^b	4.20	0.026
5 SF/20 WM	5	–	20	–	HAPC 2 + NaOH ^b	3.94	0.049
5 SF/30 WM	5	–	30	–	HAPC 2 + NaOH ^b	3.41	0.028
5 SF/20 OK	5	–	–	20	HAPC 2 + NaOH ^b	3.94	0.042
5 SF/30 OK	5	–	–	30	HAPC 2 + NaOH ^b	3.41	0.026

^a The alkali content is calculated considering the alkalis from the PC and NaOH added to the mixing water, if any (i.e., alkalis from the SF and FA are disregarded for the purpose of calculations).

^b HAPC 2 and NaOH added to the mixing water.

^c Blends of HAPC 2 and LAPC.

Table 3
Mixing proportion of the paste samples (mass%)

Mix	PC (%)		SF (%)	FA (%)	
	HAPC 1	HAPC 2		FM	OK
PC 1	100	—	—	—	—
PC 2	—	100	—	—	—
25 FM	75	—	—	25	—
50 FM	50	—	—	50	—
25 OK	75	—	—	—	25
50 OK	50	—	—	—	50
5 SF	—	95	5	—	—
5 SF/10 FM	—	85	5	10	—
5 SF/15 FM	—	80	5	15	—
5 SF/20 OK	—	75	5	—	20
5 SF/30 OK	—	65	5	—	30
10 SF/20 OK	—	70	10	—	20

NaOH to the mixing water. Table 2 shows the combination of materials tested and the expansion values for concrete prisms at 2 years.

2.3. Pore solution analysis

Paste samples were prepared using PC, PC with SF, PC with FA and ternary blends of PC, SF and FA. All the samples were prepared at a W/CM ratio of 0.5. The HAPC 1 was used with the paste samples containing FA while HAPC 2 was used with the SF and ternary blends samples. This is because the pastes containing SF and ternary blends were prepared at a later stage during the project and HAPC 1 was no longer available. Table 3 shows the combinations of materials tested in this study. Pastes were mixed using a high-speed, high-shear food blender. The duration of mixing was 3 min (three periods of mixing of 1 min each with a rest period of 1 min after each minute of mixing). Samples were cast, sealed in 50 × 100-mm polyethylene cylinders and rotated at a speed of 12 rpm for the first 24 h after casting to prevent segregation. The sealed samples were then stored

over water at room temperature ($\approx 23^\circ\text{C}$) until testing. Upon testing, samples were demoulded and broken into fragments (5–20 mm). Some of the fragments were squeezed for pore solution extraction using the method described by Barneyback and Diamond [8]. Hydroxyl ion concentrations of the extracted solutions were determined by potentiometric titration with 0.05 N H_2SO_4 solution, while sodium and potassium ion concentrations were determined by flame photometry.

2.4. Determination of calcium hydroxide content

Calcium hydroxide (portlandite) contents of paste samples were determined by thermogravimetry in a nitrogen environment using Perkin-Elmer 7 Series Thermal Analysis System at a heating rate of $10^\circ\text{C}/\text{min}$. Samples were tested in a temperature range of 30–950 $^\circ\text{C}$; portlandite decomposed between 400 and 530 $^\circ\text{C}$.

3. Results

3.1. Expansion results

Figs. 1–3 show the expansion values of concrete prism samples containing low-, moderate- and high-calcium FA (FM, WM and OK, respectively) and samples containing ternary blends of the same ashes with 5% SF. The 2-year expansion criterion of the CSA, 0.04%, is also shown on the graphs (the 2-year expansion values for various mixes are given in Table 2). As shown in Fig. 1, 15% and 20% of the FM, on their own, were effective in reducing the expansion compared with the control sample. The sample containing 20% FM almost met the 0.04% expansion criterion of the CSA ($0.043\% \approx 0.04\%$). Further reduction in the expansion was achieved by adding 5% SF, the 5 SF/15 FM mix reduced the expansion to 0.026% compared with 0.083%

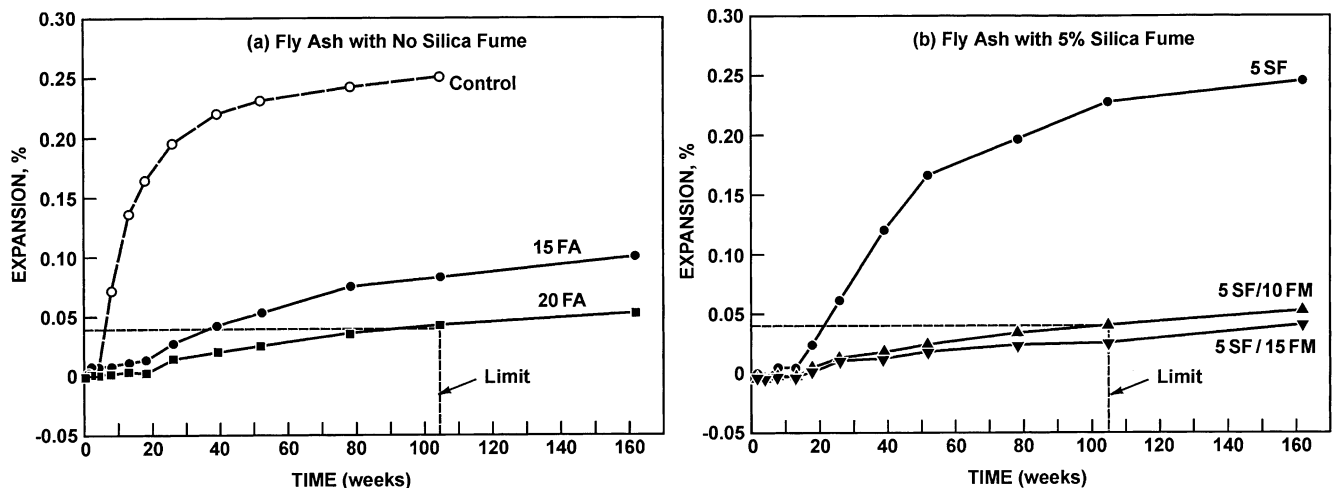


Fig. 1. Expansion results for low-calcium FA (FM).

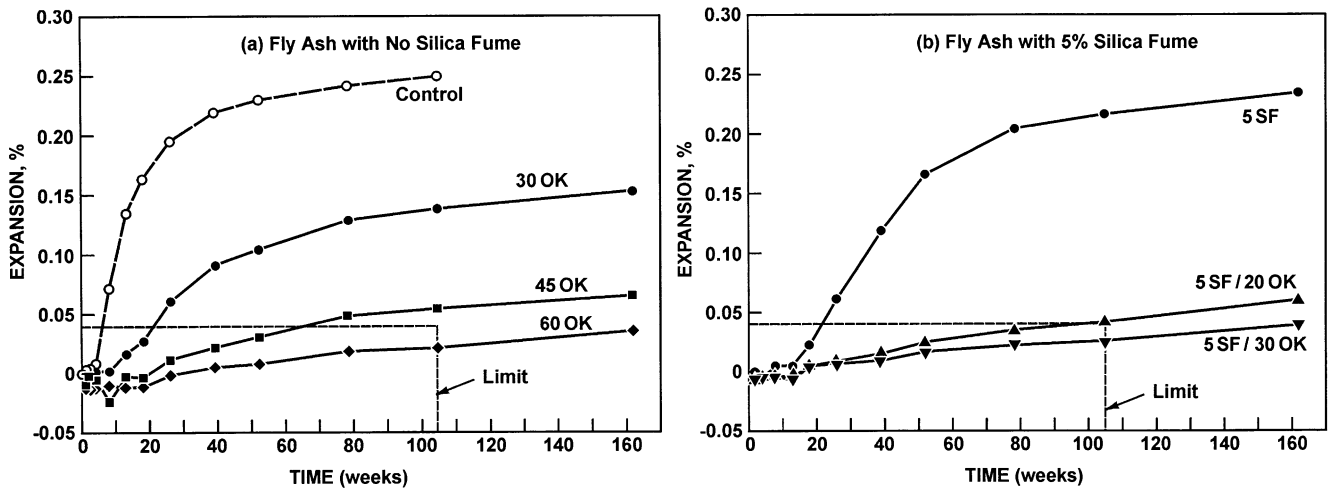


Fig. 2. Expansion results for high-calcium FA (OK).

and 0.043% for the 15 FM and 20 FM mixes, respectively. Also, the 2-year expansion of the 5 SF/10 FM mix was much lower than the mix containing 15% FM (0.041% versus 0.083%). The 20 FM and 5 SF/10 FM mixes showed identical expansion curves up to the age of 3 years. The expansion value of the 5 SF/15 FM mix at 3 years was still lower than the 0.04% expansion criterion of the CSA. The late rates of expansion (between 2 and 3 years) of the ternary blend prisms were similar to those of the samples containing FM on its own. The graph also shows that 5% SF on its own, despite delaying the initial onset of expansion, did not have a significant effect on mitigating the ultimate expansion, when compared to the control sample without SF (or FA).

The beneficial effect of using ternary blends of SF and FA is more noticeable with high-calcium FA than it is with low-calcium FA. Fig. 2 shows the expansion of concrete prisms containing OK and the reduction in the expansion achieved

by introducing 5% SF into the mix. The 2-year expansion value was reduced from 0.138% to 0.026% by adding 5% SF to the sample containing 30% ash; the value is significantly lower than the expansion value of the control sample. The 3-year expansion of the 5 SF/30 OK mix was lower than the 0.04% CSA expansion criterion. The expansion curve for the 5 SF/30 OK mix was similar to that of the 60 OK mix.

The expansion of the concrete prisms containing the high-alkali FA (WM) is shown in Fig. 3. As with the case for OK, 30% and 40% of the WM were not able to meet the 0.04% expansion criterion while 5% SF and 30% WM (5 SF/30 WM mix) showed an expansion value of 0.028% after 2 years. However, the 3-year expansion of this sample exceeded the 0.04% expansion criterion (0.045% after 3 years).

Fig. 4 summarises the 2-year expansion of concrete prisms containing different levels of SF and FA. One group of the results represents the expansion of samples containing

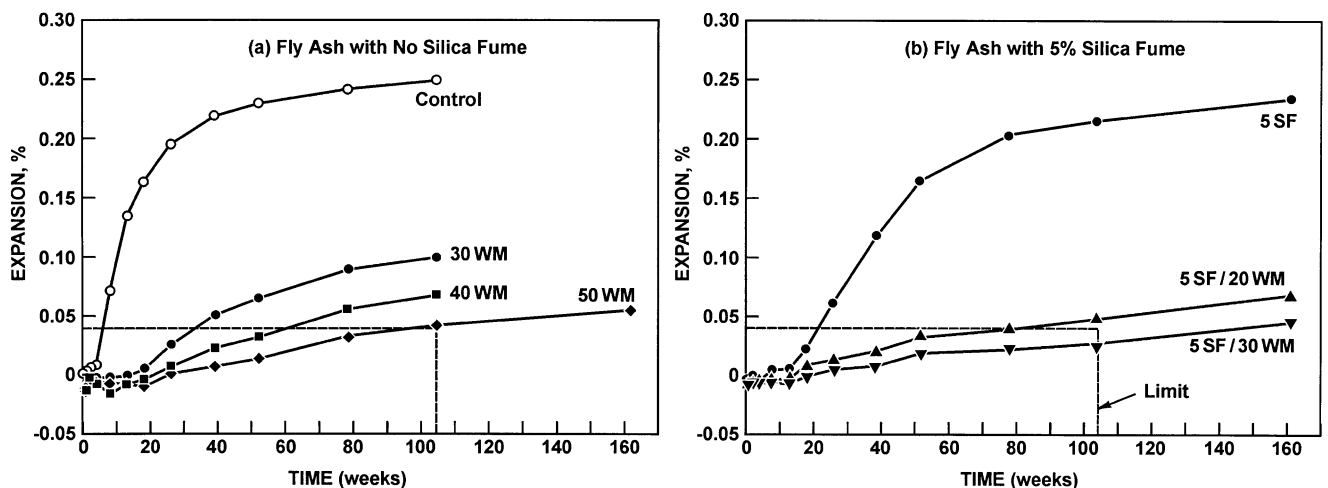


Fig. 3. Expansion results for high-alkali FA (WM).

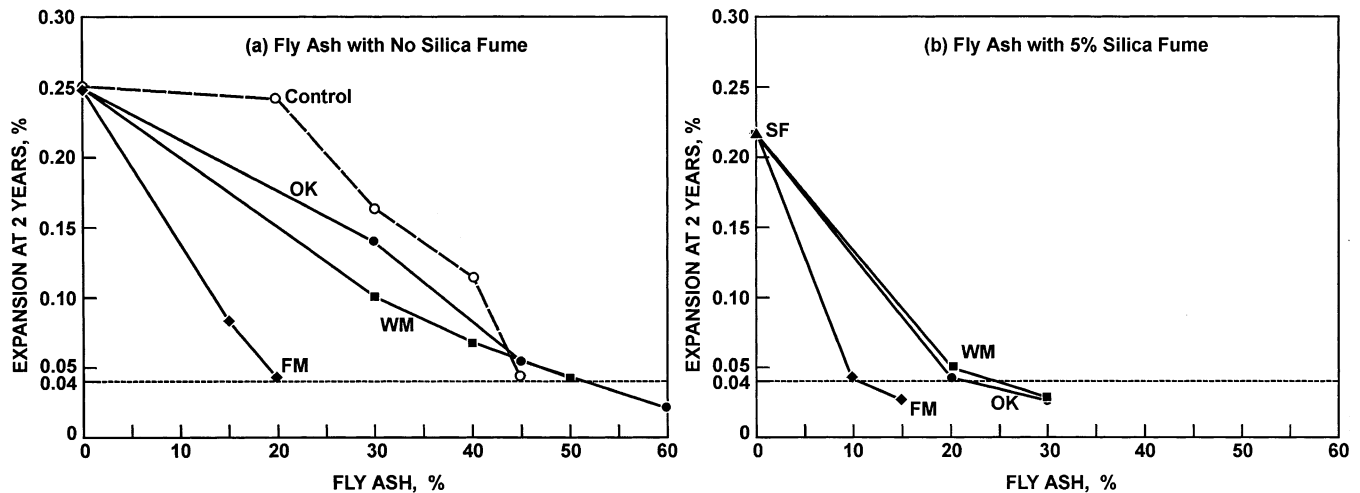


Fig. 4. Two-year expansion of concrete prisms samples containing PC, PC+SF, PC+FA and PC+SF+FA.

only FA (Fig. 4a) and the other group represents samples containing FA and 5% SF (Fig. 4b). The horizontal line on the graph shows the CSA expansion criterion at 2 years. Also shown on the graph are the expansion values of the control samples made with an alkali content of $5.25 \text{ kg/m}^3 \text{ Na}_2\text{O}_e$ (the value at 0% FA) and those made with alkali dilution corresponding to the FA levels (on the x-axis). The graph shows that for the same replacement level of FA, samples containing 5% SF are significantly more effective in reducing the expansion than those containing only FA. This phenomenon was found for all the tested materials and replacement levels. Moreover, the expansion values of the mixtures containing SF and FA are much lower than those of the control samples made with alkali dilution equivalent to the FA level. In other words, the effect of SF/FA combination is far beyond the alkali dilution achieved by replacing part of PC with pozzolans (assuming no alkalis

contributed by the pozzolans). It is worth noting that samples containing only FA did also show reduction in the expansion compared to control samples made with alkali dilution equivalent to the FA level; however, the reduction in the expansion was not as significant as that found with the samples containing SF/FA.

3.2. Chemistry of pore solution

For all the paste samples tested up to the age of 3 years, the OH^- ion concentrations were almost the same as the sum of alkali cations ($\text{OH}^- \approx \text{Na}^+ + \text{K}^+$). Fig. 5 shows the concentrations of OH^- ions versus that of alkalis ($\text{Na}^+ + \text{K}^+$) for all the samples tested up to the age of 3 years. Pore solutions extracted after 1 day (20–24 h) showed higher ($\text{Na}^+ + \text{K}^+$) than OH^- ion concentration, which suggests the presence of anions other than OH^- in solution at that early age (e.g. sulphate).

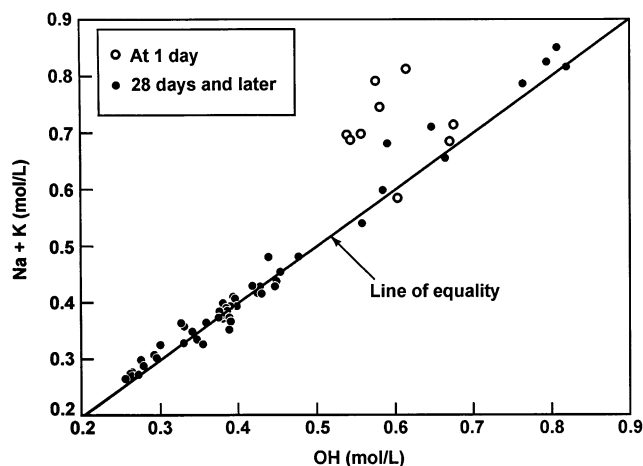


Fig. 5. Hydroxyl ion concentration versus the sum of alkali cations ($\text{Na}^+ + \text{K}^+$) in the pore solution of the paste samples at ages from 1 day (20–24 h) to 3 years.

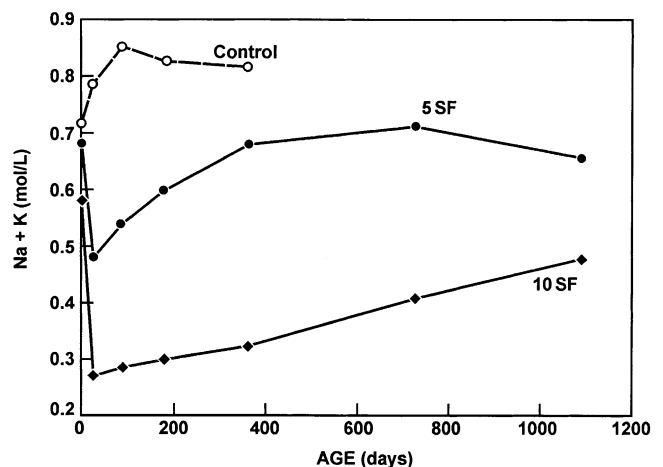


Fig. 6. Effect of SF on the alkalinity of pore solution of pastes, represented by the sum of alkali cations in the pore solution.

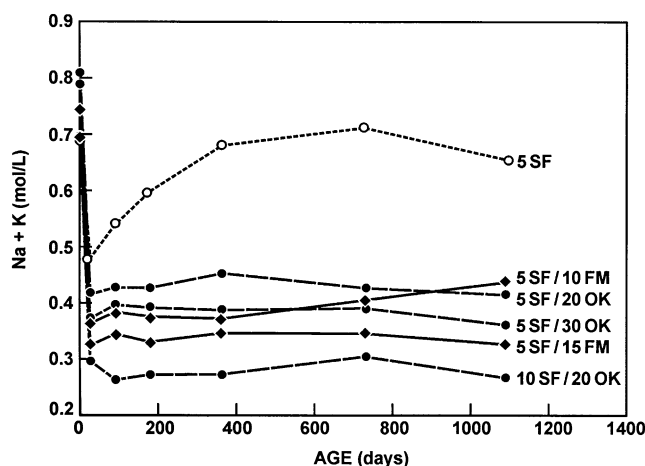


Fig. 7. Effect of SF/FA combinations on the alkalinity of pore solution of pastes, represented by the sum of alkali cations in the pore solution.

The evolution of pore solution chemistry with time is illustrated in Fig. 6 for pastes containing SF and in Fig. 7 for pastes containing ternary blends. SF significantly reduced the pore solution alkalinity at early ages (up to 28 days); however, much of the alkalis initially removed from solution are released back into solution at later ages. Similar observation was reported by other researchers [9], however, they reported that the released alkalis was significant only when the samples were cured at elevated temperature (38 °C). This trend was not found for pastes containing FA only [10]. FA of different chemical compositions showed a reduction in pore solution alkalinity with time at ages later than 90 days; however, the levels of alkalinity were dependant upon the FA composition [10]. When both SF and FA were used together, the beneficial effect of using SF (low early pore solution alkalinity) was achieved without the shortfall of raising the pore solution alkalinity at later age, Fig. 7. Indeed, the low pore solution alkalinity of the samples containing 5% SF with moderate levels of FA remained unchanged up to the age of 3 years. The exception to the behaviour of the ternary blends was the mixture with 5% SF and just 10% of the FM. With this relatively low level of FA, there appears to be a slow release of alkali to the pore solution at ages beyond 1 year. However, the effect is far less marked than that observed in mixes with SF only.

Fig. 8 shows the pore solution alkalinity, expressed as the sum of ($\text{Na}^+ + \text{K}^+$), of paste samples containing FA and FA/SF after 2 years. Both groups of samples were cast with HAPC; the alkali content of the cement used with mixes containing FA as the only replacement material was 1.09% Na_2O_e (HAPC 1) while that for the PC used with ternary blends was 1.00% (HAPC 2). The alkali concentrations ($\text{Na}^+ + \text{K}^+$) of the pore solution extracted from the control samples (without SF or FA) at 2 years were 0.90 and 0.82 mol/L for the cements with alkali contents of 1.09% and 1.0% Na_2O_e , respectively. The graph shows that for any type and level of pozzolan, samples containing ternary

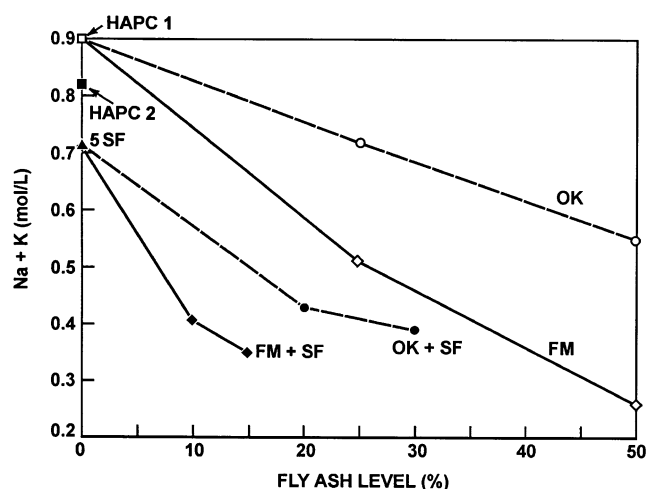


Fig. 8. Effect of FA, SF and combinations of SF/FA on pore solution alkalinity at 2 years.

blends (with 5% SF) yielded pore solution of considerably lower alkalinity. A similar observation was found when the expansion of the two groups (samples containing FA and those containing ternary blends) were compared (Fig. 4). This indicates that the considerably low expansion observed for concrete samples containing ternary blend is probably a result of the low pore solution alkalinity.

3.3. Portlandite content

The portlandite contents, $\text{Ca}(\text{OH})_2$, of the paste samples are given in Table 4. The SF consumed more $\text{Ca}(\text{OH})_2$ than FA during the pozzolanic reaction. This is attributable to the ultra fineness and high amorphous silica content of the SF. The reduction in $\text{Ca}(\text{OH})_2$ in the system has been claimed by some researchers [4,5,11,12] to have a positive role in reducing the risk of expansion due to ASR. However, it is not possible to explain the differences in expansion between mixes on the basis of differences in the portlandite content and, in the authors opinion, the role of

Table 4
 $\text{Ca}(\text{OH})_2$ content of the mature paste samples expressed as percentages of the ignited mass at 950 °C

Mix	Age (years)	$\text{Ca}(\text{OH})_2$ (%)
PC 2	1	19.2
25 FM	3	10.4
50 FM	3	4.0
25 OK	3	11.2
50 OK	3	0.2
5 SF	1	12.8
10 SF	1	8.6
5 SF/10 FM	1	10.6
5 SF/15 FM	1	10.3
5 SF/20 OK	1	9.2
5 SF/30 OK	1	7.4
10 SF/20 OK	1	3.1

portlandite consumption in these tests is secondary to that of pore solution alkalinity.

4. Discussion

The expansion data show that adding 5% SF to concrete containing FA significantly reduces the 2-year expansion due to ASR. The three selected ashes examined in this study showed the beneficial effects of adding SF to both low and high-calcium FA. The effect is more pronounced with the high-calcium ash.

Many of the concrete mixtures that met the 2-year expansion limit of 0.04% continued to expand beyond this period and actually exceeded 0.04% after 3 years. The implication of this slow long-term expansion in terms of field performance needs to be evaluated. Perhaps some comfort could be taken in the observation that the mix with 20% Type F FA (FM) exhibits a trend of continuing long-term expansion in these test conditions. Such levels of FA have proven long-term field performance (i.e., 25 years) in concrete even when combined with highly reactive aggregate and HAPC [6]. Based on such field performance, the authors feel confident that combinations of materials that meet the 0.04% limit at 2 years in the accelerated test condition will have a very low risk of exhibiting deleterious expansion under normal field conditions, even if such mixtures display some low level of expansion beyond the 2-year testing period in the laboratory. Ternary blends, particularly the blends that showed expansion lower than 0.04% even after 3 years, may constitute a promising approach for producing durable concrete with long service life. In addition to their efficiency in suppressing ASR, these ternary blends produce concrete with excellent fresh and hardened properties. To further evaluate their long-term performance, the expansions of concrete prisms containing ternary blends are still being monitored at the University of Toronto.

The high-alkali WM was not as effective as the low-alkali FA in mitigating the expansion when used with 5% SF; a higher level of SF (say 7%) may be required to put such an FA to work more effectively.

The combination of SF and FA showed a synergistic effect on concrete expansion. In other words, the reduction in expansion resulting from a blend of SF and FA is greater than the reduction due to SF plus the reduction due to FA when they are used on their own. The synergistic effect of the SF/FA blend is illustrated in the following example:

Mix	Expansion at 2 years (%)	Reduction in expansion (%)
PC 1 (control)	0.250	—
5 SF	0.216	$0.250 - 0.216 = 0.034$
30 OK	0.138	$0.250 - 0.138 = 0.112$
5 SF/30 OK	0.026	$0.250 - 0.026 = 0.224$

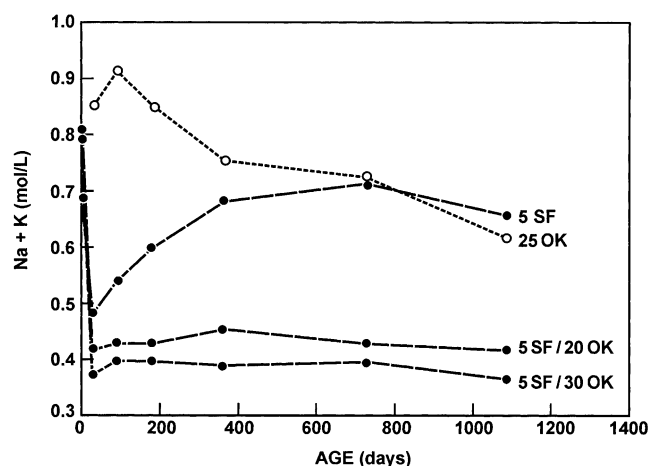


Fig. 9. Effect of SF, OK and combination of SK/OK on pore solution alkalinity.

Sum of reductions in the expansion due to 5% SF and 30% OK = $0.034 + 0.112 = 0.146\%$, while the reduction due to ternary blend containing 5% SF and 30% OK (5 SF/30 OK mix) is 0.224%.

The results in Fig. 6 indicate that SF rapidly binds alkalis probably due to a reaction very similar to ASR. However, these alkalis are later released and it is thought that this is due to the initial ASR product exchanging alkalis for calcium. When FA is present in addition to SF, these alkalis are not returned to the pore solution. This may be because there is less calcium available (i.e. consumption of $\text{Ca}(\text{OH})_2$ by pozzolanic reaction of FA) in these systems that stifles the cation exchange process or it may simply be that the alkalis released from the initial SF reaction products are sequestered by the FA or its hydration products. Regardless of the mechanism, the presence of both SF and FA results in a low pore solution alkalinity at both early and late ages. In other words, the synergy that exists between SF and FA can be explained on the basis of their different time-dependant effects. SF is very effective in reducing the alkalinity at early age whereas FA becomes increasingly effective at later ages. The combination of the two materials produces a pore solution that is initially low in alkalis and remains that way. This is illustrated in Fig. 9, which shows the evolution of pore solution composition of paste samples containing 5% SF, 25% OK or combinations of the two materials (5 SF/20 OK and 5 SF/30 OK mixes). Note that the OK reduces the pore solution alkalinity slowly over a long period of time (i.e., the OH ion concentration was reduced from 0.85 mol/L at 6 months to 0.62 mol/L at 3 years), but it appears to be effective in maintaining low alkalinity in the pore solution if SF is present to reduce the alkalinity at early ages.

Fig. 10 shows the expansion of concrete prisms at 2 years plotted against the pore solution composition of pastes of the same age and produced from the same blends of cementitious materials. The graph includes a control mixture (with no pozzolans), ternary blends and binary blends of PC

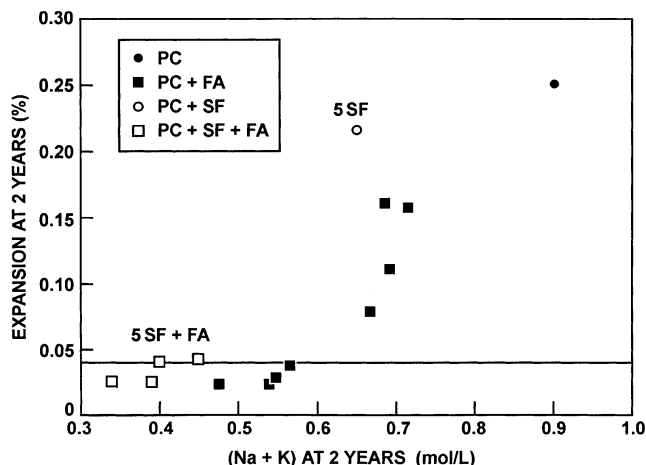


Fig. 10. Relation between pore solution alkalinity of paste samples and the 2-year expansion of concrete prisms containing same combination of materials.

and FA or SF. The authors are aware that pore solutions extracted from pastes cured at 23 °C do not necessarily reflect the composition of pore solutions of concrete containing reactive aggregate and cured at 38 °C. However, the authors believe that pore solutions extracted from the paste samples containing different cementing combinations provide a reasonable indication of the relative levels of pore solution alkalinity of the concrete containing the same cementing combinations. Generally, combinations of materials that were effective in keeping the pore solution to below 0.60 mol/L of alkali at 2 years were also effective in suppressing expansion to 0.04% or below. A similar value (0.65 mol/L) was suggested by other researchers [5] for mixtures containing binary blends of PC and FA. As the alkalinity of the paste increases above 0.60 mol/L there is an increase in the expansion of concrete prisms although clearly there is no unique relationship for the different mixtures studied. Indeed, the concrete mix with 5% SF had a higher expansion than might be expected solely on the basis of the pore solution alkalinity of an equivalent paste sample. This might indicate that alkalis released later in the life of concrete have a more deleterious effect than those available as the concrete is hardening and developing strength at earlier ages. Similar but less marked behaviour was exhibited by the ternary blends; mixes with SF and FA expanded slightly more than may be expected based on pore solution results (compare data for SF/FA with those for FA only) although ultimate expansions are still low. This might be explained on the basis of a more refined pore structure in the ternary mixes [13], which provides less space to accommodate expansion. However, the refined pore structure may also be expected to be beneficial in terms of reducing ion diffusion and hence the rate of reaction. Alternatively, it is possible that in the case of concrete, there is a competition between the reactive aggregates and the FA hydration products to react with or bind the alkalis released from the SF products of hydration. The result is that part of the

released alkalis reacts with the aggregates rather than having all the released alkalis bound by the FA hydrates, as in the case of paste samples. The alkalis that react with the aggregate contribute to the expansion resulting in slightly higher expansion for samples containing ternary blends.

5. Conclusions

- Practical levels of SF and FA introduced into HAPC systems were found to be effective in reducing the expansion due to ASR to levels <0.04% after 3 years.
- Pastes samples containing SF achieved low pore solution alkalinity at early ages. After 28 days, there was a gradual but sustained increase in the alkalinity up to 2 or 3 years.
- The shortfall of the increased pore solution alkalinity with age obtained for cementitious systems containing SF was overcome by using FA together with the SF. That is, ternary blends resulted in pore solution of low alkalinity at early ages with no increases at later ages.
- The expansion of concrete prisms containing ternary blends could be explained based on the alkalinity of pore solution.

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References

- [1] M.D.A. Thomas, Review of the effect of fly ash and slag on alkali–aggregate reaction in concrete, Building Research Establishment Report BR314, Construction Research Communications, Watford, UK, 1996.
- [2] M.D.A. Thomas, R.F. Bleszynski, The use of silica fume to control expansion due to alkali–aggregate reactivity in concrete—a review, in: J. Skalny, S. Mindess (Eds.), *Materials Science of Concrete*, American Ceramics Society, Westerville, OH, 2001.
- [3] M.H. Shehata, M.D.A. Thomas, The effects of fly ash composition on the expansion of concrete due to alkali–silica reaction, *Cem. Concr. Res.* 30 (2000) 1063–1072.
- [4] J. Duchesne, M.-A. Berube, The effectiveness of supplementary cementing materials in suppressing expansion due to ASR: another look at reaction mechanisms: Part 1. Concrete expansion and portlandite depletion, *Cem. Concr. Res.* 24 (1) (1994) 73–82.
- [5] J. Duchesne, M.-A. Berube, The effectiveness of supplementary cementing materials in suppressing expansion due to ASR: another look at reaction mechanisms: Part 2. Pore solution chemistry, *Cem. Concr. Res.* 24 (2) (1994) 221–230.
- [6] M.D.A. Thomas, Field studies of fly ash concrete structures containing reactive aggregates, *Mag. Concr. Res.* 48 (177) (1996) 265–279.
- [7] B. Fournier, A. Bilodeau, V.M. Malhotra, CANMET/Industry research consortium on alkali–aggregate reactivity, in: *CANMET/ACI Interna-*

- tional Workshop on Alkali-Aggregate Reactions in Concrete, Natural Resources, Canada, 1995, pp. 169–180.
- [8] R.S. Barneyback Jr, S. Diamond, Expression and analysis of pore fluids from hardened cement paste and mortars, *Cem. Concr. Res.* 11 (1981) 279–285.
- [9] M.-A. Berube, J. Duchesne, J. Frenette, Influence of storage conditions and concrete composition on the effectiveness of different silica fume against ASR, Proceedings of the 6th CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Bangkok, Thailand, May, Supplementary Book, Canmet, Ottawa, 1998, pp. 1127–1147.
- [10] M.H. Shehata, M.D.A. Thomas, R.F. Bleszynski, The effect of fly ash composition on the chemistry of pore solution, *Cem. Concr. Res.* 29 (1999) 1915–1920.
- [11] M.D.A. Thomas, The role calcium in alkali–silica reaction, in: M. Cohen (Ed.), *Materials Science of Concrete—The Sidney Diamond Symposium*, American Ceramics Society, Westerville, OH, 1998, pp. 325–337.
- [12] J.A. Larbi, J.M. Bijen, Effect of mineral admixtures on the cement paste–aggregate interface, in: V.M. Malhotra (Ed.), *Proceedings of the 4th International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete*, Am. Concr. Inst., SP 132, vol. 1, American Concrete Institute, Detroit, MI, 1992, pp. 655–669.
- [13] M.D.A. Thomas, M.H. Shehata, Use of Multicomponent Cementitious Systems in High-Performance Concrete, *Use of Multicomponent Cementitious Systems in High-Performance Concrete*, Am. Concr. Inst., SP 189-17, American Concrete Institute, Detroit, MI, 2000, pp. 295–309 (January).