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Use of ternary cementitious systems containing silica fume and fly ash in concrete

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Abstract

This paper reports the results from laboratory studies on the durability of concrete that contains ternary blends of portland cement, silica fume, and a wide range of fly ashes. Previous work has shown that high CaO fly ashes are generally less effective in controlling alkali silica reactivity (ASR) and sulfate attack compared with Class F or low lime fly ashes. Indeed, in this study it was shown that replacement levels of up to 60% were required to control expansion due to ASR with some fly ashes. However, combinations of relatively small levels of silica fume (e.g., 3 to 6%) and moderate levels of high CaO fly ash (20 to 30%) were very effective in reducing expansion due to ASR and also produced a high level of sulphate resistance. Concretes made with these proportions generally show excellent fresh and hardened properties since the combination of silica fume and fly ash is somewhat synergistic. For instance, fly ash appears to compensate for some of the workability problems often associated with the use of higher levels of silica fume, whereas the silica fume appears to compensate for the relatively low early strength of fly ash concrete. Diffusion testing indicates that concrete produced with ternary cementitious blends has a very high resistance to the penetration of chloride ions. Furthermore, these data indicate that the diffusivity of the concrete that contains ternary blends continues to decrease with age. The reductions are very significant and have a considerable effect on the predicted service life of reinforced concrete elements exposed to chloride environments.

Keywords: Durability; Fly ash; Silica fume; Concrete

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1. Introduction

The benefits of using either fly ash or silica fume in concrete in partial replacement for portland cement are fairly well established. However, both materials have certain shortfalls and neither could be described as a panacea for all concrete problems. Silica fume, while imparting significant contributions to concrete strength and chemical resistance, can create increases in water demand, placing difficulties, and plastic shrinkage problems in concrete if not properly used and can present handling difficulties in the raw state. These factors coupled with the increased cost of silica fume compared with portland cement and other pozzolans or slag have been barriers to its wider use in routine "day-to-day" concreting jobs. Deficiencies associated with the use of fly ash in concrete depend on the nature of the fly ash being considered. The recently revised Canadian Standards Association (CSA) specification for fly ash, CSA A23.5, divides fly ash into three classes depending on its calcium content, in recognition of the difference in behaviour between low and high lime fly ashes [1]. These classes are as follows:

Type F, low calcium, <8% CaO
Type CI, intermediate calcium, 8–20% CaO
Type CH, high calcium, >20% CaO

Low CaO fly ashes generally provide good resistance to alkali-silica reaction (ASR) and sulphate attack. However, strength development at early ages is typically slower than that in conventional portland cement content, especially at higher levels of replacement. High CaO fly ashes, on the other hand, are less efficient in suppressing expansion due to ASR or sulphate action, but generally react faster than low CaO fly ashes and have less negative impact on the early strength of concrete and are less sensitive to inadequate curing [1]. Most fly ashes, regardless of composition, tend to reduce the water demand of concrete and increase its resistance to fluid flow and the ionic diffusion. The beneficial effects of fly ash on permeability and diffusivity tend to become more apparent with time (maturity), especially in the case of the more slowly reacting low CaO fly ashes [2].

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The combination of silica fume and fly ash in a ternary cement system (i.e., portland cement being the third component) should result in a number of synergistic effects, some of which are obvious or intuitive, as follows:

- Silica fume compensates for low early strength of concrete with low CaO fly ash.
- Fly ash increases long-term strength development of silica fume concrete.
- Fly ash offsets increased water demand of silica fume.
- Silica fume reduces the normally high levels of high CaO fly ash required for sulphate resistance and ASR prevention.
- Very high resistance to chloride ion penetration can be obtained with ternary blends.
- Low CaO fly ash compensates for higher heat release from Type 10SF cement.
- The relatively low cost of fly ash offsets the increased cost of silica fume.

This paper synthesizes data from a number of different research projects being carried out at the University of Toronto to demonstrate the effects of ternary cementitious blends containing fly ash and silica fume on the strength and durability of concrete.

2. Strength

Fig. 1 shows the strength development of concrete mixes with various combinations of portland cement, low CaO fly ash, and silica fume. The water-to-cementitious materials range from 0.26 to 0.35 and air content ranges from 4.5 to 7.0%, making direct comparison of absolute strength values between mixes difficult. However, a comparison of the shapes of the curves in Fig. 1 provides an indication of the individual contributions of the fly ash and silica fume in the ternary blend. Using silica fume increases the strength of concrete at all ages, but it is apparent that much of the increase is realized at early ages and the rate of strength development at later ages is similar for silica fume concrete and plain portland cement concrete. Low CaO fly ash has the opposite effect, contributing little to strength at early ages, but significantly enhancing strength at later ages. The combination of silica fume and low CaO fly ash results in concrete with improved early age and long-term strength development.

3. Chloride diffusion

Chloride diffusion testing was carried out using an electrical migration test that has been described in detail elsewhere [3]. In this test the saturated test sample is "sand-

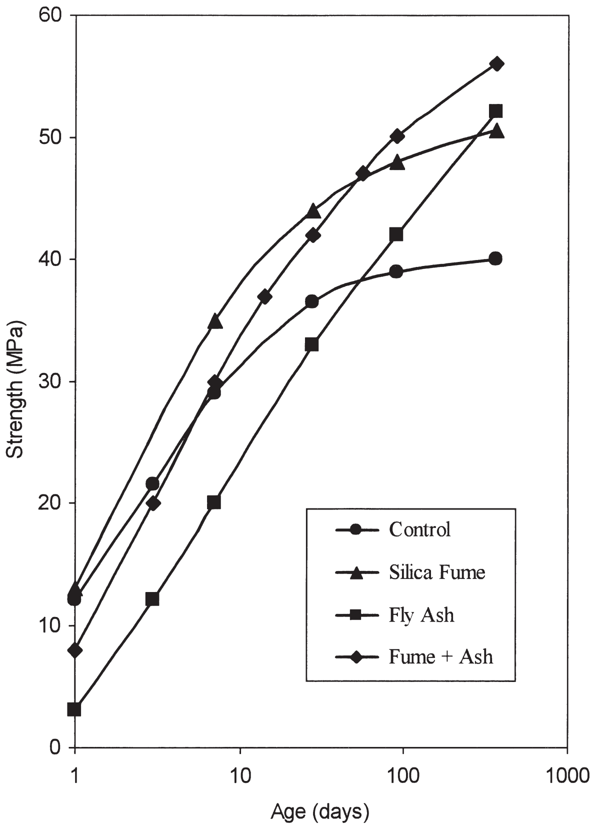

Fig. 1. Compressive strength development in concrete effect of silica fume and low lime fly ash.

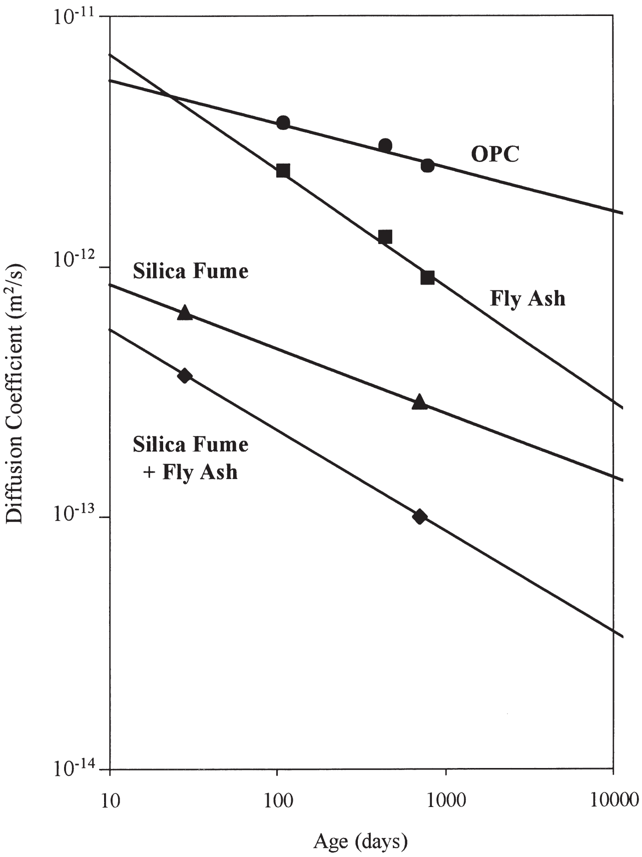

Fig. 2. Effect of silica fume and fly ash on chloride diffusivity (electrical migration test).

Table 1
Effect of fly ash and silica fume on chloride diffusion coefficients

Cement type	D_{28} (m^2/s)	m
Control	4.3×10^{-12}	0.23
25% fly ash	4.4×10^{-12}	0.62
Type 10SF[a] (8% silica fume)	6.6×10^{-13}	0.25
Type 10SF + 25% fly ash	3.7×10^{-13}	0.40

[a] Type 10SF = blended cement with 8% silica fume interground with portland cement.

wiched" between two chambers, which contain an electrolyte and a stainless steel electrode. The solutions used were 1 M NaCl + 0.3 M NaOH as the catholyte and 0.3 M NaOH as the anolyte. A potential difference of 12 V (corrected for polarization losses at the electrodes) was applied between the two chambers and the chloride concentration of the anodic chamber was monitored. The diffusion coefficient can be calculated from either the chloride flux at steady state or the "time of breakthrough," which is the time taken for chlorides to migrate through the sample. The latter approach was used in this study.

The individual contributions of silica fume and fly ash to the early age and long-term strength are consistent with data for the same concretes from chloride diffusion tests shown in Fig. 2. The silica fume produces a reduction in the measured diffusion coefficient at early ages, whereas the presence of fly ash results in a continuous reduction in diffusivity with time. The relationships shown in Fig. 2 can be represented by Eq. (1):

$$D_t = D_{28} \cdot \left(\frac{t_{28}}{t}\right)^m \tag{1}$$

where D_t = diffusion coefficient at time t, D_{28} = diffusion coefficient at time t_{28} = 28 days, and m = constant.

Values of D_{28} and m for the concretes tested are shown in Table 1. These relationships can then be used in mathematical models to predict the chloride ingress at various times under different environmental conditions. This assumes that the diffusivity will continue to decrease at the rate shown in Fig. 2 throughout the modelling period. Although data in this figure only represent concrete up to 800 days old, recent studies on concrete taken from 30-year-old structures indicate that the transport properties continue to decay at the rates predicted from earlier age tests [4]. Figs. 3 and 4 show predicted chloride profiles in concrete assuming a constant surface concentration of 1% (chlorides by mass of concrete) and that the dominant transport mechanism is diffusion. The figures demonstrate the considerable benefits of incorporating either silica fume or fly ash in concrete exposed to chloride environments. At early ages (e.g., 5 years) concrete containing 8% silica fume provides increased resistance to

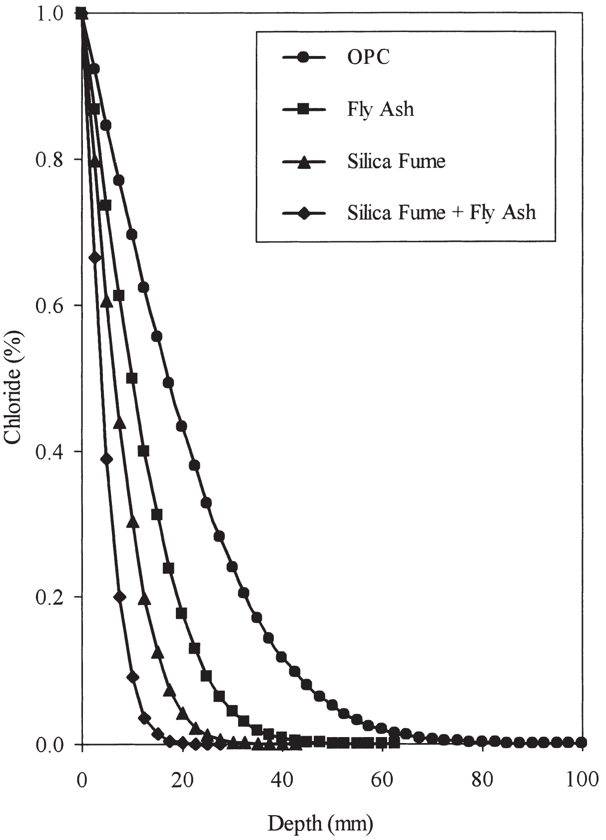

Fig. 3. Effect of silica fume and fly ash on chloride ingress at 5 years.

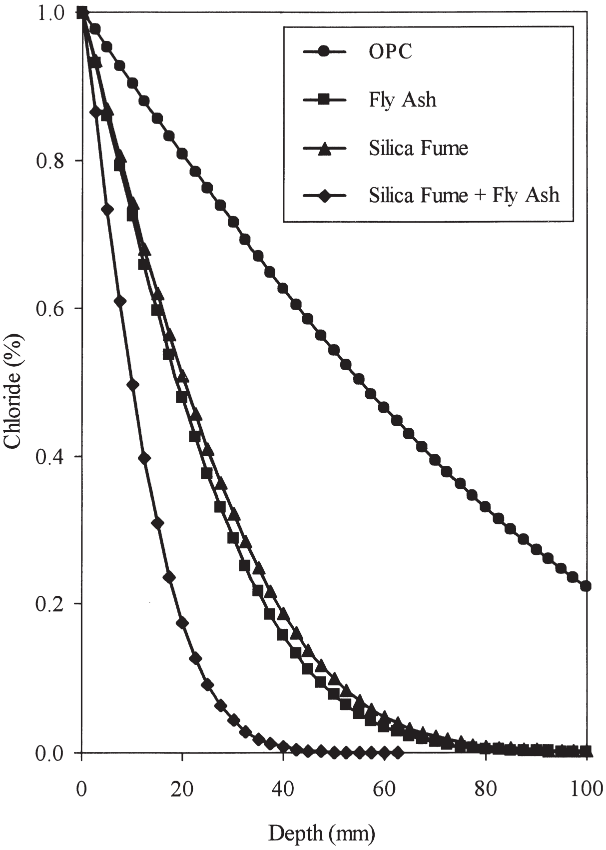

Fig. 4. Effect of silica fume and fly ash on chloride ingress at 100 years.

chlorides compared to concrete with 25% fly ash due to its lower initial diffusion coefficient. However, at later ages differences between the chloride profiles for the two concretes become smaller due to the greater reductions in diffusivity with time for fly ash ($m = 0.62$) compared with silica fume ($m = 0.25$). The concrete with the ternary blend has the benefit of a low diffusivity at early age and relatively large decay in diffusivity with time ($m = 0.40$), which combine to enhance the resistance to chloride penetration compared with concrete containing either fly ash or silica fume (Fig. 4).

4. ASR

A number of investigators using a variety of test methods have demonstrated that ASTM Class C fly ashes do not provide the same level of protection against ASR as ASTM Class F fly ashes [5–10]. In Canada, the efficacy of pozzolans and slag are tested using a standard concrete prism test (CSA A23.2 Test 14A) with the testing period extended to 2 years [11].

Fig. 5 shows 2-year expansion data for concrete containing reactive siliceous limestone (Spratt), high alkali cement (raised to 1.25% Na_2O_e), and various levels of different fly ashes. These fly ashes all had alkali contents below 3.0% Na_2O_e, but varied in calcium content (6.4–27.7% CaO). The higher calcium fly ashes are clearly less efficient in terms of controlling expansion; they require levels of replacement in the range of 50% to meet the CSA expansion limit of 0.04% at 2 years, compared with approximately 25% for the lower calcium fly ashes. Testing by others [12] has shown that up to 12% silica fume may be required to control the expansion to an acceptable level under the same test conditions.

Replacement levels of 50% high CaO fly ash or 12% silica fume may not be practical for many concreting applications and may not be permitted in many specifications. However, combinations of lesser amounts of these materials have been shown to be very effective in controlling ASR expansion, as shown by the data for concrete prisms in Fig. 6. Concrete containing 5% silica fume and between 20 to 30% high calcium (27.7% CaO) was found to meet the CSA limit (0.04% at 2 years) when combined with the highly reactive Spratt aggregate and high alkali cement.

Fig. 7 shows the 14-day expansion data from modified accelerated mortar bar tests (ASTM C 1260) incorporating the same Spratt aggregate together with high alkali cement (0.95% Na_2O_e). Previous studies [13,14] have shown that those levels of pozzolan or slag that reduce the 14-day expansion to 0.10% in this accelerated test are also effective in limiting the 2-year expansion of concrete prisms to 0.04%. Using the accelerated test it was found that either 60% high

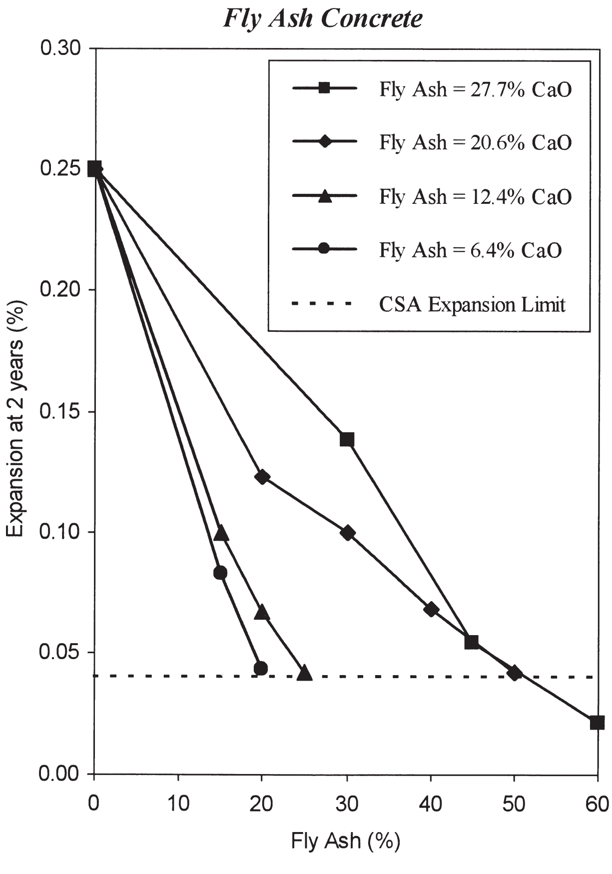

Fig. 5. Effect of fly ash calcium content on expansion due to ASR.

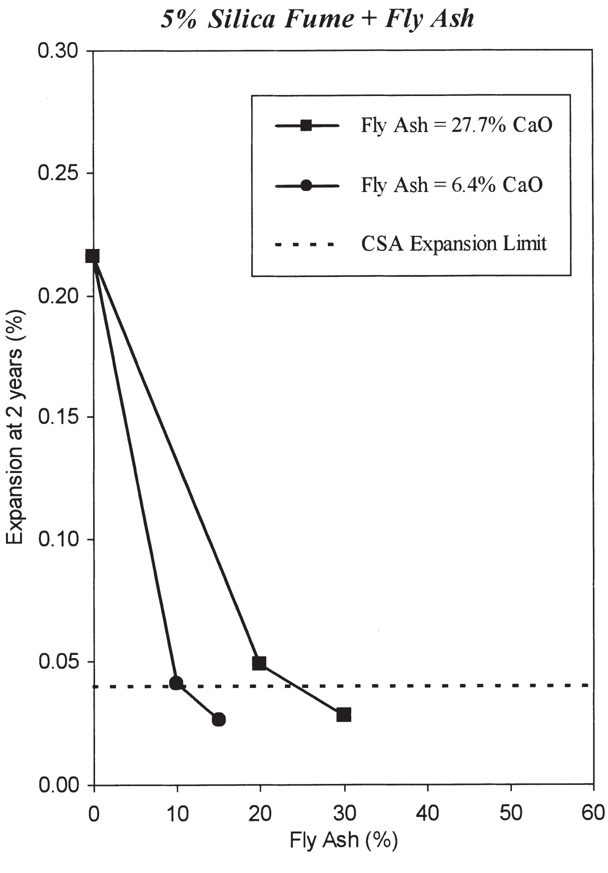

Fig. 6. Effect of silica fume and fly ash on expansion due to ASR.

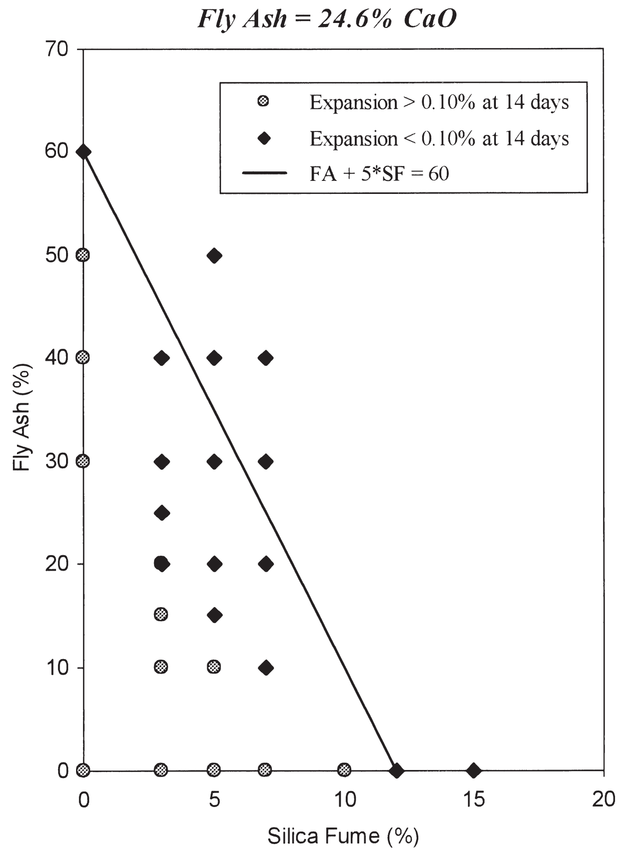

Fig. 7. Effect of ternary blends on expansion due to ASR in ASTCM C 1260 with Spratt aggregate.

CaO or 12% silica fume was required to reduce the expansion to 0.10% at 14 days. If these two materials made the same contribution to reducing ASR expansion when used in combination as they made when used individually, then one would expect the combination to work provided the following condition was satisfied [see Eq. (2)]:

$$FA + 5 \cdot (SF \geqslant 60) \qquad (2)$$

where FA = level of fly ash (%) and SF = level of silica fume (%).

Fig. 7 shows that many of the combinations tested fail to satisfy the condition in Eq. (2), but still reduce expansion to less than 0.10% at 14 days, indicating that there is a synergistic effect when the fly ash and silica fume are combined (i.e., the effect of the combination is greater than the sum of the individual contributions).

One of the mechanisms by which fly ash controls ASR is by increasing the alkali binding capacity of the hydrates and thus reducing the alkalinity of the pore solution. In pore solution studies carried out by Diamond and Lopez-Flores [6], it was shown that high calcium fly ashes are not as effective as low calcium ashes in reducing the alkali concentration of the pore solution. Other workers [15,16] have shown that the "available alkali" (as determined by ASTM C 311 testing procedures or modified versions thereof) in fly ash, as a proportion of the total alkali, increases as the calcium content of the fly ash increases. In recent studies at the University of Toronto [17] it was shown that there was a relationship between the pore solution alkalinity in pastes containing high alkali cement and 25% fly ash and the parameter $(CaO + 10 \cdot Na_2O_e)/SiO_2$ calculated from the oxide composition of the fly ash. Selected data from the study by Shehata et al. [17] for low and high CaO fly are shown in Fig. 8. It can be seen that the level of fly ash required to reduce the alkalinity of the pore solution to a certain level increases with the higher calcium content of the fly ash. Indeed there is a marked similarity between the trend in OH^- concentration and fly ash replacement (Fig. 8) and the trend in expansion and fly ash replacement (Fig. 5).

Fig. 8 also shows the OH^- concentration in the pore solution extracted from pastes containing combinations of silica fume and fly ash. The use of silica fume has a dramatic effect on the pore solution composition, reducing the OH^- concentration from 0.98 M in control specimens to 0.59 and 0.30 M in specimens containing 5 and 10% silica fume, respectively. The further addition of 20 to 30% high CaO fly ash to pastes containing silica fume has a relatively minor effect on the pore solution alkalinity. Indeed, pastes containing 5% silica fume and either 20 or 30% high CaO fly ash have a higher concentration of OH^- than pastes with

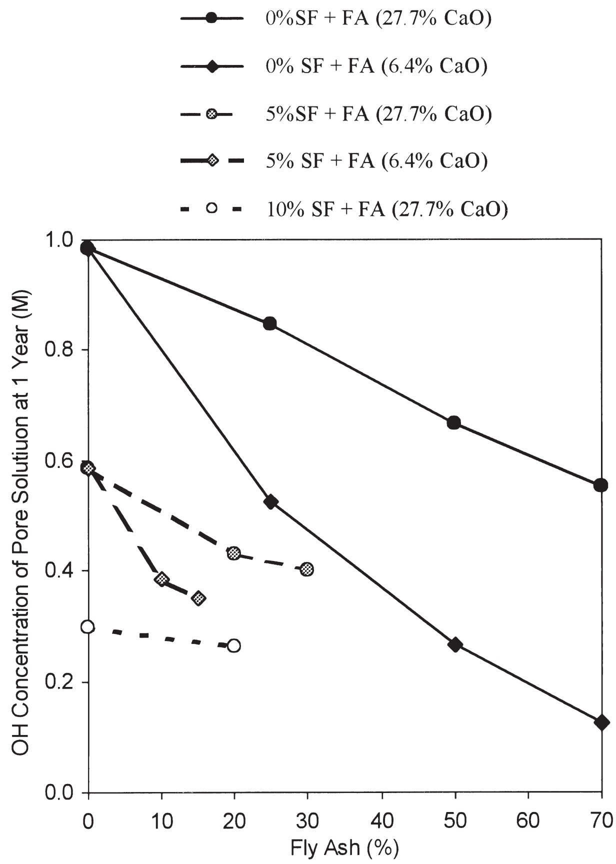

Fig. 8. Effect of silica fume and fly ash on pore solution composition.

10% silica fume only. In spite of this, the ternary blends are more effective in controlling ASR expansion than 10% silica fume used on its own. Thus the expansion behaviour cannot be explained simply on the basis of pore solution composition.

5. Sulphate resistance

The reduced efficacy of high CaO fly ashes in controlling sulphate attack was first documented by Dunstan [18] and later by others [19,20]. Fig. 9 shows data from the University of Toronto using ASTM C 1012 for determining the sulphate resistance of various fly ashes when combined at a replacement level of either 20 or 40% with a high C_3A cement. Low CaO fly ashes exhibited a high sulphate resistance and intermediate calcium ashes showed high to moderate resistance, whereas high calcium fly ashes showed variable performance, with some ashes giving higher expansions than the control mortars. The level of replacement had no consistent effect on the test results with high CaO fly ashes. These data are generally consistent with the findings of others [18–20] and the recommendations of ACI 232 [21]. The ACI document states that fly ashes with less than 15% CaO will improve sulphate resistance, but that ashes with higher calcium contents should be tested. The performance of fly ashes tested at the University of Toronto could not be predicted using Dunstan's R-factor [18].

Fig. 10 shows the expansion behaviour of selected mortar bars. The combination of 20 or 40% of a high CaO fly ash with high C_3A cement showed inferior performance to the control specimens without fly ash. The deterioration of the specimens with fly ash was manifested in a different manner to the control mortar. Specimens without ash fly expanded rapidly beyond 3 months, reaching an expansion of 1.49% after 1 year in Na_2SO_4 solution, after which the mortar bars were extensively cracked but still intact. Mortar bars with high CaO fly ash expanded more rapidly (especially at the higher level of replacement) and essentially disintegrated to the extent that they could no longer be measured beyond 3 to 6 months even though they had expanded by less than 0.40%. The addition of relatively small amounts of silica fume (i.e., 3% by mass of cementitious material) to mortars containing high CaO fly ash reduced expansion significantly: 1-year values were less than 0.10%. The expansion of the mortars containing the ternary blend was still higher than that of mortars with only 20% of a low lime (ASTM Class F) fly ash. Furthermore, there was some indication of surface softening in the ternary cement mortars after 1 year.

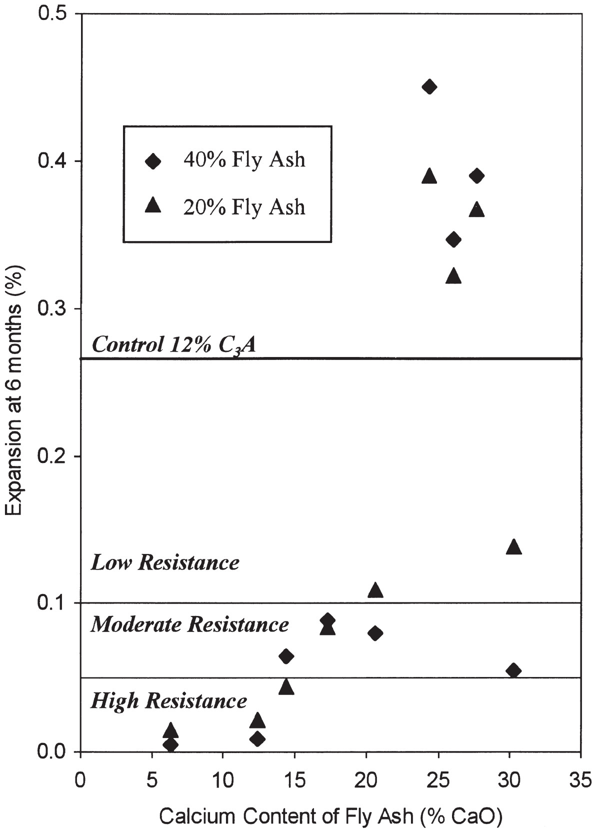

Fig. 9. Effect of fly ash calcium content on sulphate resistance (ASTM C 1012).

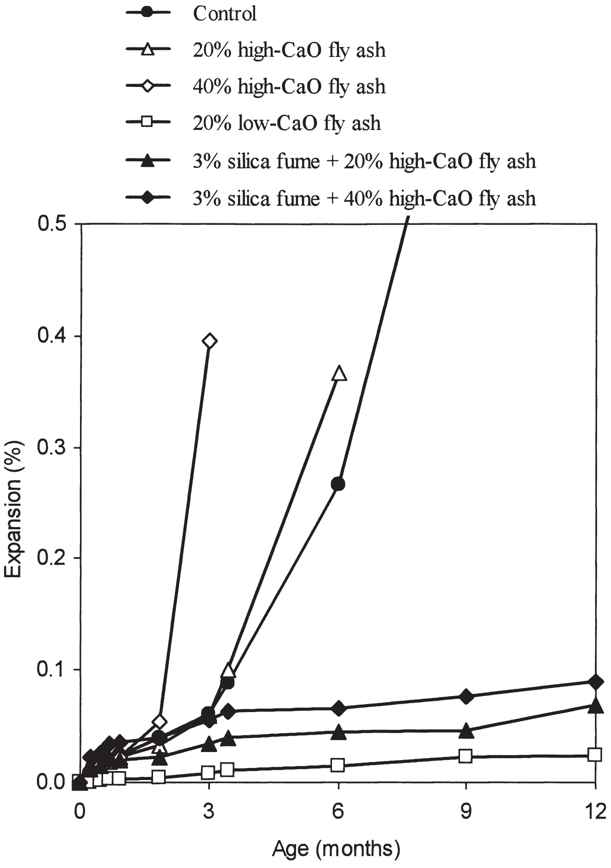

Fig. 10. Effect of silica fume and fly ash on sulphate resistance (ASTM C 1012).

The reduced sulphate resistance of mortars or concretes containing high calcium fly ash has been ascribed to reaction of sulphates with C_3A or calcium-aluminate glass in the fly ash, or with calcium-aluminate hydrates (e.g., gehlenite) produced by hydration of the fly ash [18,20]. An alternative mechanism put forward by Mehta suggests that it is the ratio of reactive alumina to sulphate in the cement-fly ash blend that determines its resistance to sulphate [22]. If this ratio is high, the formation of monosulphate and calcium-aluminate hydrates is favoured and, on subsequent immersion in sulphate solution, these phases will be converted to ettringite, resulting in deleterious expansion. If there is an excess of sulphate in the system, ettringite will be the stable phase prior to immersion in sulphate solution and the subsequent exposure will not be harmful.

It is not clear how the addition of small quantities of silica fume effect the vulnerability of the hydrates produced by the reaction of the high CaO fly ash. It is possible that the increased availability of silica results in the formation of more stable calcium-alumino-silicates. Alternatively, the increased resistance of the ternary blends may simply be a result of pore structure refinements and increased resistance to the penetration of sulphates. Further testing is underway at the University of Toronto to elucidate the mechanisms behind the sulphate resistance of these ternary blends.

6. Summary

It is apparent that ternary cementitious blends of portland cement, silica fume, and fly ash offer significant advantages over binary blends and even greater enhancements over plain portland cement. The combination of silica fume and low CaO fly ash is complementary: the silica fume improves the early age performance of concrete with the fly ash continuously refining the properties of the hardened concrete as it matures. In terms of durability, such blends are vastly superior to plain portland cement concrete. In some cases, price differences between the individual components may allow the ternary blend to compete with straight portland cement on the basis of material costs.

The shortfalls of high CaO fly ash in terms of controlling ASR and sulphate resistance can be compensated for by the incorporation of relatively small quantities of silica fume. Combinations of 3 to 5% silica fume with 20 to 30% high CaO show satisfactory performance in both ASR and sulphate expansion tests. Such combinations produce concrete with generally excellent properties and offset the problems associated with using the increased amounts of high CaO fly ash or silica fume required when these materials are used individually. However, at this stage it is not clear how the two materials "work together" to improve the durability. For example, the reduced ASR expansion cannot be explained solely on the basis of simple pore solution tests and the mechanisms behind the improved sulphate resistance have not been resolved. It is possible that much of these benefits are attributed to reductions in permeability and ionic diffusivity in the system. Consequently, the tests described in this paper will be continued to determine whether the improvements are maintained in the long term.

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