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The effects of fly ash composition on the chemistry of pore solution in hydrated cement pastes

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Abstract

This paper reports the findings of an investigation to determine the influence of fly ash composition on the evolution of the pore solution chemistry in Portland cement/fly ash systems. Twelve fly ashes, selected to represent the wide range of composition of North American ashes, were used in the study. In addition to pore solution expression and analysis, inner hydration products were analyzed using energy-dispersive X-ray analysis. The study shows that the alkalinity of pore solution increases as the calcium and alkali content of the fly ash increase, and decreases as the silica content of the ash increases. However, there is no consistent trend between the composition of the inner calcium-silicate hydrate and fly ash composition.

Keywords: Alkali-aggregate reaction; Pore solution; Fly ash; EDS; Calcium-silicate hydrate (C-S-H)

1. Introduction

The effect of fly ash on the pore solution of hydrated cement paste has been studied by a number of investigators since Diamond first reported data for two Danish fly ashes in 1981 [1–8]. Most of the published data deal with low-lime fly ashes produced from either anthracite or bituminous coals (i.e., ASTM C 618 Class F fly ash). Generally the data show that when such fly ashes are used to partially replace Portland cement, the concentration of alkali ions (Na^+ and K^+) and associated hydroxyl ions (OH^-) in the pore solution decreases significantly. The extent of this reduction depends on a number of factors, including the nature of the fly ash (e.g., fineness, glass content, and alkali availability), the level of replacement, the alkali content of the Portland cement, and age. There is comparatively little data on fly ashes of higher calcium contents typical of those produced from some sub-bituminous and lignite coals (e.g., ASTM C 618 Class C fly ash), which often have calcium contents above 20% CaO and sometimes above 30% CaO.

Diamond and Lopez-Flores [9] compared the behaviour of fly ashes from bituminous and lignite coals. The lignite ashes were characterized by very high calcium contents (>30% CaO) compared to the bituminous ashes (<4% CaO). The fly ashes were used to replace 30% of a low-alkali Portland cement (0.60% Na_2O_e) in a paste with a water/solids ratio of 0.50. Pore solution compositions were compared after 180 days of hydration. The two bituminous ashes behaved effectively as inert diluents, reducing the alkalinity of the pore solution approximately in proportion to the level of replacement. However, the three lignite ashes all increased the hydroxyl ion concentration of the pore solution compared with the control Portland cement pastes, indicating the alkalis to be readily available to the pore solution. This occurred despite the relatively low-alkali content of two of the lignite ashes compared with the bituminous ashes. Duchesne and Berube [6] reported similar differences between low- and high-calcium fly ashes. However, the high-calcium ash used in their study (21% CaO) also had a very high alkali content (8.55 Na_2O_e) and contained appreciable quantities of water-soluble thenardite (Na_2SO_4). It has also been reported that the proportion of the total alkali in fly ash that is "available," when tested in accordance with ASTM C 311, is greater in high-calcium fly ashes than in low-calcium fly ashes [10].

In the present study a wide range of North American fly ashes were used in an effort to better define the effect of ash composition, level of replacement, and maturity on the alkalinity of the pore solution in blended cement pastes. In addition, microanalysis of the inner hydration product was carried out to determine whether the differences in pore solution composition could be ascribed to the ability of these phases to bind alkalis.

2. Materials and experiments

The materials used in this study were a high-alkali Portland cement (1.09% Na_2O_e) and 12 fly ashes of different

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

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Na_2O_e[a]	TiO_2	P_2O_5	Na_2O_e[b]	LOI[c]
OPC	18.66	6.56	3.02	61.40	2.93	4.39	1.03	0.41	1.09	0.24	0.13	–	0.92
LG	41.96	19.64	20.07	5.57	1.19	0.95	2.44	0.69	2.30	0.84	0.15	1.10	3.71
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
SD	54.22	21.97	3.95	12.39	1.12	0.21	0.29	2.73	2.92	0.66	0.13	1.42	0.34
TB	40.68	21.19	4.50	15.87	3.54	2.18	0.49	8.14	8.46	0.96	0.65	3.60	0.53
C1	44.29	20.96	5.23	17.51	4.21	2.13	0.84	1.13	1.68	1.12	0.63	0.77	1.14
BD	41.3	17.35	8.06	18.37	4.22	1.02	0.76	4.85	5.35	0.60	0.33	2.43	0.16
BR	32.71	19.02	5.76	18.85	4.30	4.81	0.68	8.28	8.73	1.24	0.52	4.79	1.18
PI	38.42	20.57	5.64	20.50	4.39	1.76	0.62	2.64	3.05	1.00	0.52	1.84	2.01
C2	39.83	19.56	5.54	21.53	4.62	2.14	0.60	1.55	1.94	1.20	0.71	0.99	1.68
EW	38.22	18.43	5.72	24.61	4.72	1.55	0.44	1.39	1.68	1.42	1.04	0.94	0.18
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
CC	41.12	11.24	5.93	30.00	4.40	2.13	1.76	1.10	2.26	0.47	0.10	1.05	0.78

[a] Acid-soluble alkali.
[b] Available alkali, expressed as Na_2O_e, as per ASTM C311.
[c] Loss-on-ignition.

chemical composition. Results of chemical analyses of the cementitious materials are given in Table 1. The fly ashes were selected to provide a range of calcium and alkali contents representative of commercially available ashes in North America. Fig. 1 shows the distribution of the CaO and Na_2O_e contents of the fly ashes used in this study. The CaO contents ranged from 5 to 30%. The alkali contents of nine ashes were less than 3.1% Na_2O_e, while those of the other three ashes were in the range of 5.3 to 8.7% Na_2O_e, most of which was present as sodium.

Paste samples were prepared using selected fly ashes, namely FM, BD, and OK, at 25, 50, and 70% replacement levels and a water/cementing materials ratio of 0.5. These three ashes were selected to represent low-, moderate-, and high-calcium ashes, respectively. Paste samples prepared using the other nine fly ashes were proportioned at a replacement level of 25% and the same water/cementing materials ratio. 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 (~ 23°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 [11]. Hydroxyl ion concentrations of the extracted solutions were determined by automatic titration against 0.05 N of H_2SO_4 solution, while sodium and potassium ion concentrations were determined by flame photometry.

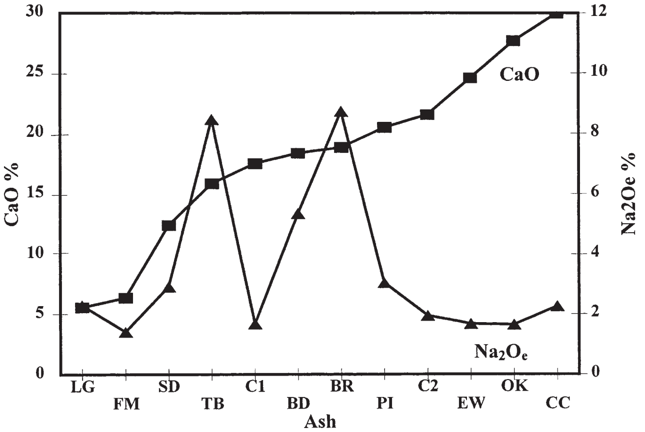

Fig. 1. Calcium and alkali contents of the fly ashes.

To investigate the change in the composition of Portland cement hydrates due to the presence of fly ash, the inner calcium-silicate hydrate (CSH) forming within the original boundaries of alite and belite grains were analyzed using energy-dispersive X-ray analysis (EDS). Secondary CSH, including that resulting from the reaction of fly ash, was not analyzed due to the intimate mixture of this phase with other hydrates. A representative fragment from the centre of each paste sample was embedded in epoxy, polished to a surface roughness of 1 μm, and coated with a thin film of carbon (200–250Å) for backscattered electron imaging and EDS. Analyses were performed on 2-year-old samples at an accelerating voltage of 20 keV and a current emission of 100 μA. An average of 50 to 70 analyses were performed for each sample to obtain statistical representative means of these products.

3. Results

3.1. Pore solution chemistry

Fig. 2 shows the OH^- ion concentration vs. the sum of alkali cations in the pore solution of all the tested samples. Except for the high-alkalinity pore solution of the 25% TB and 25% BR (see Table 1 for composition of fly ashes), samples tested at 25 and 50% replacement levels showed a good mass balance between $[OH^-]$ and $[Na^+ + K^+]$ ions. At 70% replacement levels, the pore solution contained higher concentrations of $[Na^+ + K^+]$ than $[OH^-]$. This indicates that other anions (e.g., SO_4^{2-}) are in solution in the

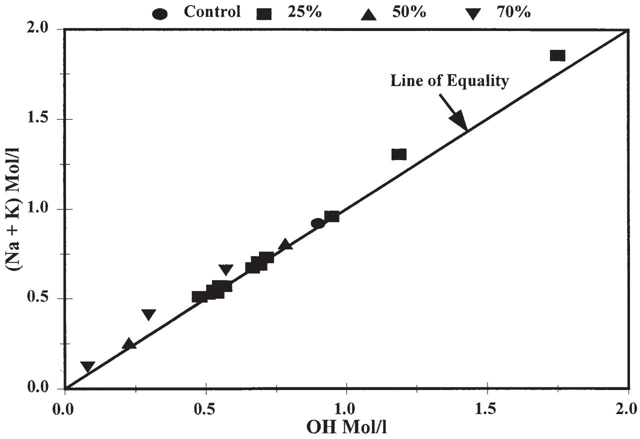

Fig. 2. OH^- vs. ($Na^+ + K^+$) ions in the pore solution of the tested samples.

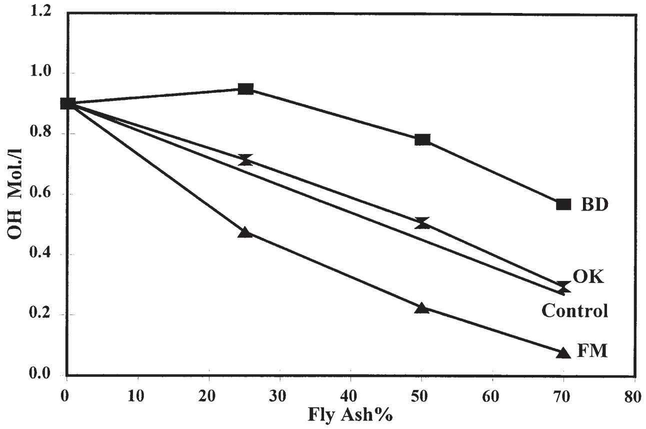

Fig. 4. Effect of level of replacement on the alkalinity of pore solution at 2 years.

pastes with 70% fly ash. Fig. 3 shows the change of pore solution alkalinity with age of the paste samples made with different fly ashes at replacement levels of 25, 50, and 70%. The hydroxyl ion concentration of pore solution in the high-alkali cement control sample varied between 0.84 and 0.98 M OH^- between 28 days and 2 years. The use of low-CaO fly ash (FM) was effective in reducing the alkalinity at all replacement levels.

Fly ash with a much higher calcium content but similar alkali content (OK) was considerably less effective in controlling the pore solution alkalinity. However, the OH^- concentration in the pastes made with this fly ash was observed to decrease with age at a faster rate than that for the pastes with the lower calcium fly ash, particularly noticeable at higher levels of replacement (e.g., 70%). The moderate-CaO fly ash (BD) did not reduce the pore solution alkalinity when used at a 25% level of replacement. This is undoubtedly due to its high-alkali content (5.35% Na_2O_e). Surprisingly, this fly ash became more effective in controlling the pore solution alkalinity at higher levels of replacement.

Fig. 4 shows the relationship between the OH^- concentration of the pore solution after 2 years of hydration and the level of replacement of the three different fly ashes (FM, BD, and OK). Also shown is the theoretical effect of replacing the Portland cement with an inert diluent (e.g., assuming a given level of replacement of cement produces the same level of reduction in the OH^- concentration). The low-CaO fly ash (FM) clearly has an effect beyond mere dilution since the reduction in alkalinity is proportionally higher than the level of replacement. The high-CaO fly ash essentially produces an effect similar to that of theoretical dilution, whereas the moderate-CaO fly ash with the high-alkali level clearly raises the pore solution alkalinity, suggesting that this fly ash contributes significant quantities of alkali to the pore solution.

Fig. 5 shows the OH^- ion concentration of the pore solution in 2-year-old paste samples with the 12 different fly ashes plotted against the CaO content of the fly ash. The two horizontal lines represent the OH^- concentration of the control sample (top) and the theoretical effect of a 25% inert diluent (bottom). Only three fly ashes fail to reduce the OH^- concentration compared to the control. These are all characterized by having high-alkali contents ($\geqslant$5.35%

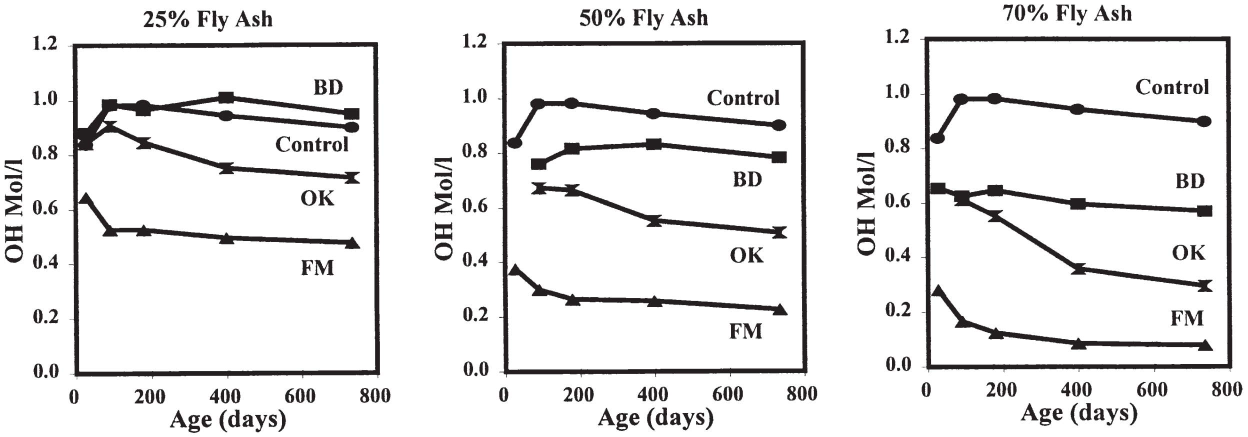

Fig. 3. Effect of age on pore solution alkalinity of pastes made with FM, BD, and OK fly ashes at 25, 50, and 70% replacement levels.

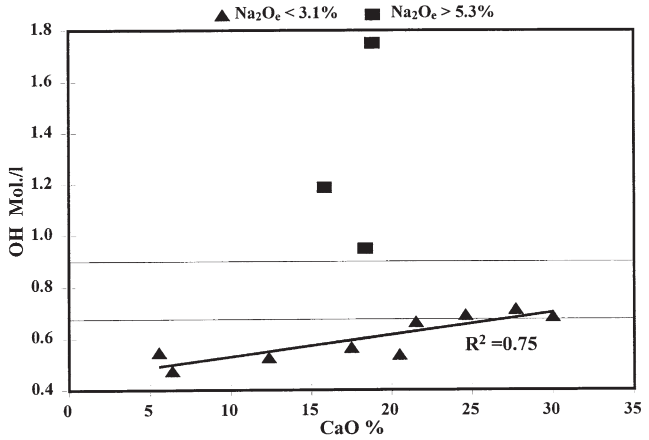

Fig. 5. Effect of calcium content of fly ash on pore solution alkalinity (25% fly ash at 2 years).

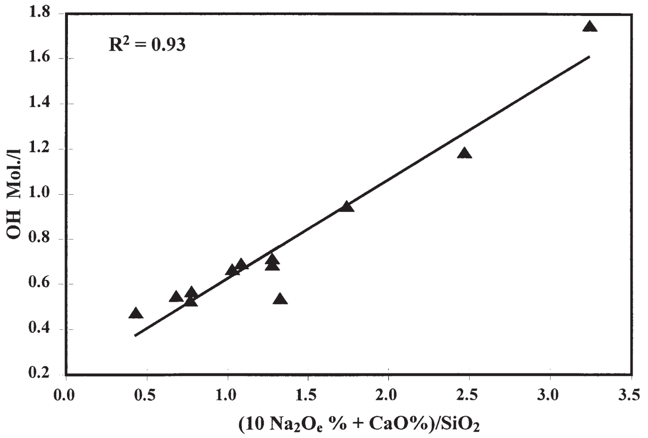

Fig. 7. Effect of alkali, calcium, and silica contents of fly ash on pore solution alkalinity (25% fly ash at 2 years).

Na_2O_e). If these high-alkali fly ashes are disregarded, a general trend of increasing pore solution alkalinity with increasing calcium content (%CaO) of the fly ash is observed. To better correlate pore solution alkalinity with fly ash composition, the alkali content (%Na_2O_e) of the fly ash needs to be accounted for. This is shown in Fig. 6, where the OH^- concentration of the pore solution is plotted against the compositional parameter, $CaO + 10 \times Na_2O_e$, of the fly ash. Further improvements in the correlation were obtained by including the silica content (%SiO_2) of the fly ash in the parameter $(CaO + 10 \times Na_2O_e)/SiO_2$, as shown in Fig. 7.

3.2. Composition of the inner hydrates

Table 2 shows the results of EDS analysis for the inner CSH formed within the original boundaries of alite and belite grains in five 2-year-old cement paste samples.

The relation between the Ca/Si and (K + Na)/Si atomic ratios of the inner CSH of the tested samples are shown in Fig. 8. The Ca/Si ratio of the CSH in the fly ash samples was, in every case, lower than that in the control samples and this lower ratio was associated with increased alkali (Na + K) levels. The expected trend between the Ca/Si ratio of the hydrates in the pastes containing fly ash and the CaO content of the raw fly ash was not observed. Furthermore, the lower pore solution alkalinity observed for pastes with low-CaO fly ash could not be ascribed to the increased ability of the inner product CSH to bind hydrates. Indeed, the CSH in the pastes with the high-CaO fly ashes (OK and EW) had higher amounts of alkali compared with the low-CaO fly ashes (FM and SD).

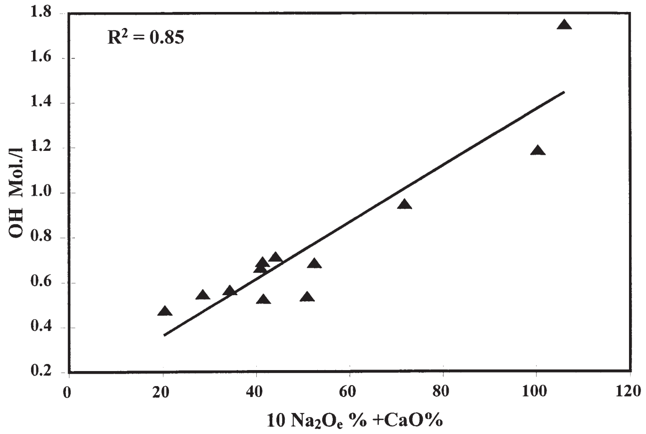

Fig. 6. Effect of alkali and calcium contents of fly ash on pore solution alkalinity (25% fly ash at 2 years).

4. Discussion

It is well established that fly ash is an effective means of controlling expansion due to alkali-silica reaction (ASR), provided it is used in sufficient quantity. The “safe level” of fly ash required depends on a number of factors, including the composition of the fly ash, level of alkali in the concrete (e.g., from Portland cement), nature of the reactive aggregate, and the exposure conditions [12]. One of the accepted mechanisms by which fly ash reduces the risk of damage due to ASR is by reducing the alkalinity of the pore solution and thus the concentration of one of the initial reaction products (i.e., OH^- ions). It is clear from this study that the efficacy of fly ash in this role is strongly influenced by its chemical composition. Not surprisingly, high-alkali fly ashes tend to be less effective in reducing pore solution alkalinity.

However, for fly ashes of low- to moderate-alkali content (e.g., $\leq 3.1\%$ Na_2O_e), the ability of fly ash to lower the availability of alkali and hydroxyl ions in solution depends on the calcium and, to a lesser extent, silica content of the individual fly ash. Other factors, such as mineralogical (e.g., glass content) and physical (e.g., fineness) properties of the fly ash, are also likely to have an influence, but were not examined in this study.

The trends in pore solution composition were consistent with data from concrete prism expansion tests carried out in

Table 2
Atomic composition (atomic %) of inner hydrates after 2 years

		Na		Si		K		Ca		Ca/Si		
Sample	No. of Analyses	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Na + K
Control	50	0.28	0.09	12.4	0.51	0.21	0.11	23.9	0.91	1.93	0.14	0.50
FM 25%	67	0.33	0.08	12.9	0.64	0.35	0.18	22.1	1.07	1.73	0.13	0.68
SD 25%	59	0.50	0.16	13.1	0.78	0.27	0.18	21.7	1.35	1.67	0.18	0.77
BD 25%	54	0.68	0.19	13.2	0.77	0.34	0.14	21.3	1.21	1.62	0.17	1.02
OK 25%	73	0.58	0.18	13.1	0.79	0.46	0.17	22.7	1.49	1.75	0.20	1.04
EW 25%	48	0.50	0.21	12.5	0.71	0.39	0.30	22.8	1.04	1.82	0.15	0.89

accordance with Canadian Standards Association (CSA) A23.2 Test 14A using the same suite of fly ashes in combination with a reactive siliceous limestone. Two-year expansion data for concrete with low-CaO (FM) and high-CaO (OK) fly ash are compared in Fig. 9. The tests show that approximately 20 and 50% of FM and OK fly ash, respectively, are required to reduce the expansion to the CSA acceptance limit of 0.04% at 2 years. Inspection of the data in Fig. 4 shows that the same levels of these fly ashes (i.e., 25% FM and 60% OK) result in very similar OH concentration when cast with high-alkali Portland cement; the level is in the range of 0.54 M OH^-. Generally, differences between the performance of various fly ashes in these ASR expansion tests can be explained almost entirely on the basis of pore solution effects.

The increased alkalinity in the pore solution of pastes with high-CaO fly ashes compared with low-CaO fly ashes could be a consequence of a higher proportion of the alkalis in the fly ash being released, reduced alkali binding by the hydration products, or both. It is possible that a greater proportion of alkalis in low-CaO fly ash are "fixed" in various nonreactive (crystalline) phases of the fly ash as compared with higher CaO fly ash. However, a comparison of fly ashes LG and EW shows that these fly ashes have very similar "available alkali" contents as determined by ASTM C 311 (Table 1), but LG produces a more marked reduction in the pore solution alkalinity of hydrated cement paste. The same behaviour was observed for SD and OK ashes.

Comparing C2 and LG emphasizes the effect of CaO content of the ash on pore solution chemistry. Both ashes are of similar silica and alumina contents, but LG has a slightly higher alkali content. Despite that, the pore solution alkalinity of the sample containing C2, of higher CaO content, is higher. It has been shown previously that fly ash decreases the Ca/Si ratio and increases the (Na + K)/Si ratio of inner CSH, and that this effect is partly responsible for the reduction in alkalinity of the pore solution when fly ash is present [13,14]. The EDS analysis carried out in this study indicates that while this remains the case, variations in pore solution alkalinity observed when different fly ashes were used cannot be ascribed to changes in the composition of the inner CSH. Unfortunately, this type of microanalysis does not readily lend itself to the investigation of outer CSH, due to the intimate mixing of the various phases between the cement grains.

It is quite probable that the composition of the pozzolanic reaction products vary considerably depending on the composition of the fly ash. Reactions between lime and high-CaO fly ash are likely to lead to products with higher Ca/Si ratios compared with low-CaO fly ash and this will probably influence the quantity of alkali that is incorporated in the hydrate. These effects are currently under investigation.

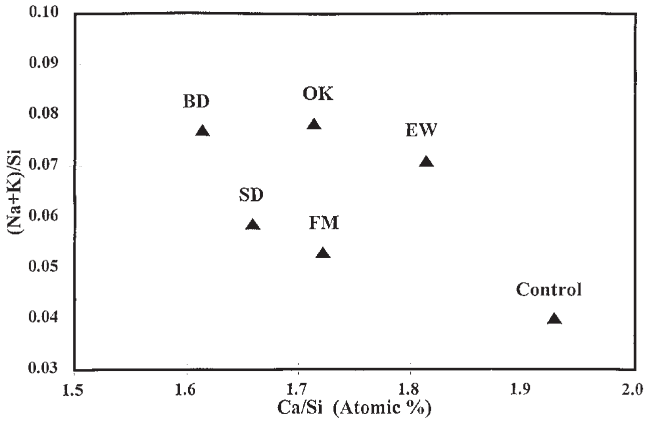

Fig. 8. The relation between Ca/Si ratio and the bound alkali of the inner hydrates of the tested Portland cement/fly ash pastes.

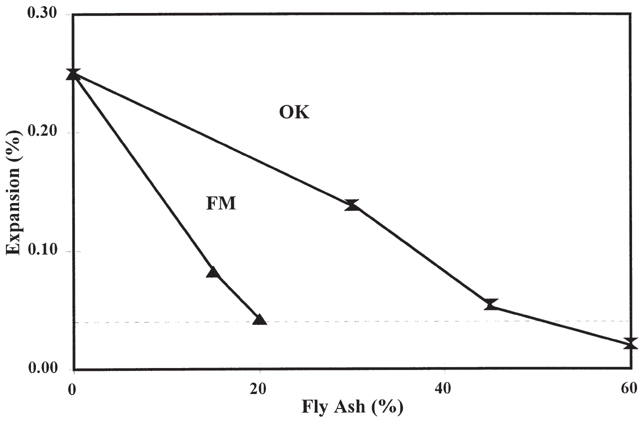

Fig. 9. Effect of fly ash on the expansion of concrete prisms.

5. Conclusions

For the samples tested in this study, it was found that:

1. The alkalinity of the pore solution extracted from hydrated pastes containing high-alkali cement and fly ash is influenced by the alkali, calcium, and silica contents of the fly ash. A reasonable relationship was found to exist between the OH^- concentration in the pore solution and the parameter $(CaO + 10 \times Na_2O_e)/SiO_2$ calculated from the chemical composition of the fly ash. Although the relationship established is for a fly ash replacement level of 25% and for pore solution composition after 2 years, it generally emphasizes the role of each parameter of the equation in affecting the pore solution chemistry. As the Na_2O_e of the ash increases, the amount of alkalis released from the ash to the pore solution is higher, yielding pore solution of higher alkalinity. CaO and SiO_2 affect the amount of silica and calcium in the system, which in turn affect the amount and/or the composition of the hydrates. The higher the silica the lower the Ca/Si ratio of the hydrates and/or the larger the amount of the hydrates. This results in higher amount of alkalis removed from solution by the hydrates (i.e., lower pore solution alkalinity). Higher calcium increases the Ca/Si ratio of the hydrates, reducing the amount of alkalis removed from the solution, which results in a high-alkali pore solution.
2. The Ca/Si ratio of the inner CSH decreases when fly ash is present. This decrease is accompanied by an increase in the alkali content of the same inner product. However, no consistent trend between the inner CSH composition and fly ash chemistry was found in this study.
3. The effect of fly ash composition on pore solution alkalinity could not be explained on the basis of alkali binding by the inner CSH.
4. The lower efficiency of high-CaO fly ash in reducing pore solution alkalinity compared with low-CaO fly ash of similar alkali content is consistent with its reduced efficacy in controlling expansion due to alkali-silica reaction.

Acknowledgments

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