

THE EFFECTS OF SILICA FUME AND FLY ASH HYDRATION PRODUCTS ON THE CHEMISTRY OF THE PORE SOLUTION AND PORTLANDITE CONSUMPTION

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ABSTRACT

This paper reports the results from studies on the effect of pozzolan (silica fume and fly ash) on the chemistry of pore solution and portlandite depletion in systems containing calcium hydroxide and pozzolan. Paste samples were prepared using calcium hydroxide, alkali hydroxide and various pozzolans including silica fume and five fly ash samples representing low, moderate and high-calcium ashes. The ratios of pozzolan to $\text{Ca}(\text{OH})_2$ and the alkalinity of the mixing water were adjusted to represent those found in systems containing Portland cement (PC) and 10% silica fume, 15% or 25% fly ash. The chemistry of the pore solution and the consumption of $\text{Ca}(\text{OH})_2$ by the pozzolanic reaction were determined at ages ranging from one day to one year. Powder XRD was performed on the raw pozzolans and the hydrated pastes. The pore solution analysis showed that for ashes of similar Na_2O_e contents, the alkalis bound in the hydration products increase as the CaO/SiO_2 ratio of the ash decrease. Silica fume was much more effective in reducing the pore solution alkalinity and $\text{Ca}(\text{OH})_2$ content than fly ash. For the same ash, portlandite consumption was found the same when the ash was used in system representing low-alkali PC or in system representing high-alkali PC. SEM examination and EDS analysis showed a difference in the structure and composition of the reaction products of low and high-calcium ashes.

Keywords: Silica fume, fly ash, pozzolanic reaction, pore solution alkalinity, portlandite consumption, alkali-silica reaction.

INTRODUCTION

The effect of fly ash and silica fume on pore solution alkalinity has been studied by a number of researchers (Diamond and Lopez-Florez 1981, Duchesne and Berube 1994, Nixon et al. 1986, Shehata et al. 1999). Silica fume and low-calcium fly ash were found effective in reducing the pore solution alkalinity while high-calcium ash was not as effective. Diamond and Lopez-Flores (1981) studied the effects of low-calcium (< 4% CaO) and high-calcium (> 30% CaO) fly ashes on pore solution alkalinity. The low-calcium ashes behaved as inert diluents, reducing the alkalinity of the pore solution approximately in proportion to the level of replacement (30%). On the other hand, 30% of the high-calcium ashes increased the hydroxyl ion concentration of the pore solution compared with the control Portland cement paste. The cement used in Diamond and Lopez-Flores study was a low-alkali cement (0.6% Na₂O_e). In another study by Shehata et al. (1999), the efficiency of fly ash in reducing pore solution alkalinity was found to be related to the calcium, silica and alkali contents of the ash. The higher the alkali and calcium and the lower the silica the lower the efficiency of the ash. The relation was established from the results of a study that involved twelve fly ashes representing a wide range of chemical compositions. However, the variations in pore solution alkalinity of different PC/FA paste samples could not be explained on the basis of the alkali content of the inner hydrates (C-S-H formed within the original boundaries of C₂S and C₃S grains). In other words, samples that contain pore solution of lower alkalinity were not necessarily associated with inner hydrates of higher alkali contents, as measured by EDS. Indeed, the alkali content of the inner hydrates of samples containing high-calcium ash was higher than that in the samples containing low-calcium ash (of similar alkali content) and yet the pore solution of the high-calcium ash samples were considerably higher. It was suggested that differences in the pore solution alkalinity might be explained on the basis of the alkali bound in the pozzolanic reaction product (i.e. lime-ash reaction product).

This paper studies the properties of the pozzolanic reaction product of fly ash or silica fume. The pozzolan were mixed with Ca(OH)₂ and mixing solutions with alkali levels similar to those of pore solutions found in Portland cement/pozzolan paste systems. The changes in the alkalinity of the pore solution and in Ca(OH)₂ content with age were monitored. The mineralogical compositions of selected pozzolans and of their hydration products were determined by powder x-ray diffraction (XRD). Selected hydrated samples were also examined using scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDS).

EXPERIMENTAL DETAILS

One silica fume, five fly ashes of various compositions and reagent grade Ca(OH)₂ were used in this study. The CaO and Na₂O_e contents of the ashes ranged from 5.57% to 30.0% and from 1.41% to 2.30%, respectively. The chemical composition of the silica fume and the fly ashes and the fineness of the fly ashes are presented in Table 1. The lime and pozzolan were mixed in proportions that represent the ratio of the pozzolan to Ca(OH)₂ in Portland cement paste systems containing pozzolan. The Portland cement is considered to produce 20% Ca(OH)₂, expressed as a percent of cement mass; this figure is based on the determined Ca(OH)₂ content of a mature control cement paste sample cured at 20-23 °C for one year. The alkalinity of the mixing water was adjusted (using NaOH and KOH) to represent the alkali content that would result from the Portland cement portion in pastes

containing pozzolan and cast at 0.5 W/CM ratio. For instance, the sum of ($\text{Na}^+ + \text{K}^+$) of a control paste sample made with high-alkali cement (1.09% Na_2O_e) and cured at 20-23 °C for 28 days was previously determined to be 0.83 Mol/l.(Shehata et al. 2000). The sum of alkali cations of the mixing water of the samples representing paste containing 25% pozzolan were designed to be $0.75 \times 0.83 \approx 0.60$ Mol/l. The ratio of Na/K ions was also adjusted to represent that found in the pore solution of the Portland cement sample.

Three groups of lime/pozzolan mixes were prepared, the first group represented pastes containing 10% SF or 15% FA made with high-alkali cement, the second represents pastes containing 2.5% SF or 15% FA made with low-alkali cement ($\approx 0.60\%$ Na_2O_e), and the third represents pastes containing 25% FA made with high-alkali cement. The low-alkali cement was assumed to produce a pore solution of OH ion concentration (M/l), after 28 days, $\approx 0.7 \times \text{Na}_2\text{O}_e\%$ of the cement ≈ 0.42 M/l, as suggested by Diamond (1989). For the purpose of comparison, samples representing pastes containing 15% fly ash and high-alkali cement were prepared with mixing water of similar alkali content as that used with samples representing pastes containing 25% FA (≈ 0.60 Mol/l). Details of the mixes (measured alkali contents of the mixing water and levels of the pozzolan) are listed in Table 2. The measured alkali contents of the mixing water were slightly different than the target values. The measured values are reported here and are also used in the analysis of the results. Due to the high surface area of the mixed material (pozzolan and hydrated lime), the mixes were cast at a W/CM ratio of 1.3 to achieve a proper mixing and consistency. The materials were mixed using high-speed, high-shear food blender. After mixing, samples were sealed in plastic cylinders and rotated at a speed of 12 rpm until hardening (to prevent segregation). The silica fume sample was removed from the rotating wheel after 24 hours while the fly ash samples were removed after 36 hours. After that, the samples were stored over water at 38°C in sealed container. An additional group of samples containing 10% SF was stored over water at 20-23 °C.

TABLE 1: Chemical Composition of the Pozzolans (Mass %)

PZ	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	Na ₂ O _e	AA ¹	P ₂ O ₅	LOI	#325 ²
SF	96.9	0.52	0.14	0.58	0.00	0.13	0.42	0.04	0.31	-	0.09	1.47	-
LG	41.9	19.6	20.1	5.57	1.19	0.95	2.44	0.69	2.30	1.10	0.15	3.71	17.8
FM	47.3	22.3	15.1	6.38	0.82	1.43	1.23	0.60	1.41	0.47	0.32	2.73	20.8
CI	44.3	21.0	5.23	17.5	4.21	2.13	0.84	1.13	1.68	0.77	0.63	1.14	13.9
OK	34.6	16.5	7.13	27.7	5.89	2.71	0.21	1.51	1.65	1.23	0.71	0.28	10.4
CC	41.1	11.2	5.93	30.0	4.40	2.13	1.76	1.10	2.26	1.05	0.10	0.78	23.8

¹ Available alkalis as per ASTM C 311.

² Percent retained on 45 microns sieve as per ASTM C 430.

Pore solution was extracted from the samples at ages from one day to one year. At ages of 7 days and later, pore solution was extracted using the apparatus described by Barneyback and Diamond (1981). At the age of 1 day, where the samples were not fully hardened, pore solutions were extracted by centrifuging and filtering; part of the sample was placed and sealed in 15-ml plastic containers and centrifuged at a speed of 7000 rpm for about 8 minutes. The solutions were then collected from the top of the samples and

filtered to remove any solid residue. Hydroxyl ion concentrations of the extracted solutions were determined by automatic titration against 0.05 N H₂SO₄ solution, while sodium and potassium ion concentrations were determined by flame photometry.

TABLE 2: Details of the Mixes - CH/PZ is the Ratio of the Ca(OH)₂ to Pozzolan.

Alkalinity of the mixing water and SCM level								
Group 1 (High Alkali)			Group 2 (Low Alkali)			Group 3 (High Alkali)		
Sample	CH/PZ ratio	Na+K M/l.	Sample	CH/PZ ratio	Na+K M/l.	Sample	CH/PZ ratio	Na+K M/l.
10% SF	1.80	0.70	2.5% SF	7.80	0.41	25% LG	0.60	0.61
15% LG	1.13	0.61	15% FM	1.13	0.33	25% FM	0.60	0.59
15% FM	1.13	0.57	15% C1	1.13	0.33	25% C1	0.60	0.61
15% C1	1.13	0.56	15% OK	1.13	0.33	25% OK	0.60	0.59
15% OK	1.13	0.57				25% CC	0.60	0.61

Calcium hydroxide contents of selected samples were determined at different ages by thermogravimetry in a nitrogen environment using a Perkin-Elmer 7 Series Thermal Analysis System at a heating rate of 10°C/minute. Samples were tested in a temperature range of 30 to 950°C; portlandite decomposed between 400 to 530°C.

Powder X-ray diffraction (XRD) patterns of selected samples of raw materials and from lime/pozzolan mixes were obtained on a Siemens D5000 X-ray diffractometer using Ni-filtered Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$).

At the age of six months, a representative fragment, from the centre of selected paste samples, was dried under vacuum in a carbon-free environment. The fragment was then embedded in epoxy, polished to a surface roughness of 1 μm and coated with a thin film of carbon (200-250 \AA) for back-scattered electron imaging and energy-dispersive x-ray analysis (EDS).

RESULTS

Chemistry of Pore Solution

The effects of pozzolan on the alkalinity of the mixing water (which represents the pore solution) are shown in Figure 1. The horizontal solid lines in the graphs represent the initial alkalinity or the sum of alkali cations in the mixing water of the FA ash mixes while the broken lines represent the same for the mixes containing SF. Figure 1-a illustrates the superior efficiency of the 10% SF in removing alkalis from the solution. The alkalis removed by 10% SF after only one day (0.11 M/l) was higher than the maximum removed by any fly ash; i.e. 25% FM which removed 0.071 M/l after 180 days. At the age of 180 days, the alkalinity of the pore solution of the sample representing 10% SF in the high-alkali system was 0.33 M/l and that of the sample representing 25% FM was 0.52 M/l., despite the higher alkalinity of the mixing water used with the SF mix. The silica fume sample cured at lower temperature, 23 °C, showed a slight reduction in the rate of alkali removal at early ages; however, samples cured at 23 °C and 38 °C achieved similar results at later ages.

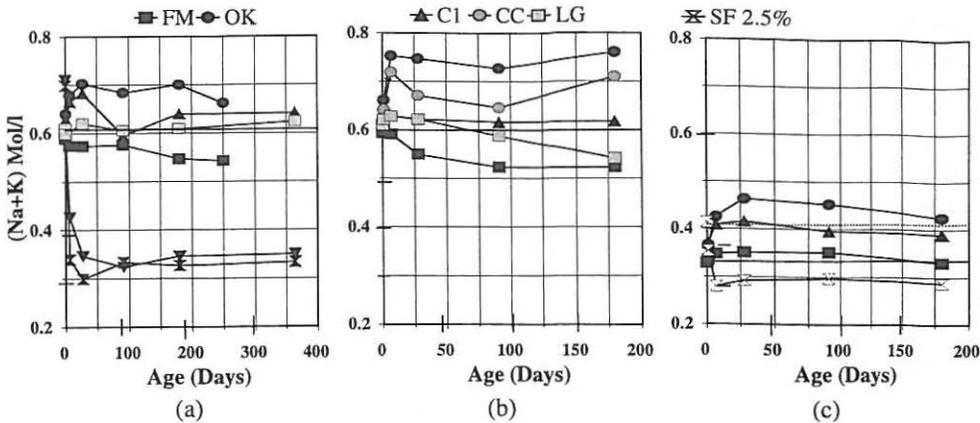


Fig.1: Effect of pozzolan on pore solution alkalinity of lime mixes representing: (a) pastes containing 10% SF and 15% FA in high-alkali system, (b) pastes containing 25% FA in high-alkali system, (c) pastes containing 2.5% SF and 15% FA in low-alkali

The low-calcium fly ash FM removed alkalis from the pore solution at both replacement levels (15% and 25%); the amount of alkalis removed was higher at 25%. The other low-calcium ash LG behaved as an inert material when used at 15% but removed alkalis at 25%, Figures 1-a and 1-b. The high-calcium fly ash (OK), of similar Na_2O_e content as the ash FM, contributed alkalis to the system. The amount of alkalis contributed was higher when the ash was used at 25% compared with that when the ash was used at 15%. The ash CC was more effective in lowering the pore solution alkalinity compared with OK although both ashes are of similar calcium content. This could be due to the higher silica content of the CC ash.

Figure 1-c shows the change in pore solution alkalinity of samples that represent pastes containing low-alkali cement and 2.5% SF or 15% fly ash. Unlike the case with high-alkali cement, Figure 1-a, the sample containing the low-calcium ash FM showed an increase in the pore solution alkalinity. Moreover, the amounts of alkalis contributed by OK and C1 ashes were higher than those contributed by the same ashes (at the same level of replacement) in systems of higher alkalinity. Contrarily to the performance of fly ash, the silica fume removed alkalis from the low-alkalinity solution even when used at a very low replacement level, 2.5%.

Portlandite Consumption

Figure 2 shows the reduction in $\text{Ca}(\text{OH})_2$ of the different mixes due to the pozzolanic reaction of the pozzolan. Figure 2-a shows mixes that represent pastes containing 15% FA or 10% SF in a high-alkali system. The horizontal solid line represent the initial $\text{Ca}(\text{OH})_2$ content (as a percentage of the ignited mass of the solids at 1050 °C) of the fly ash mixes and the dashed line represents the same for the silica fume mix. The graph shows that 10% silica fume consumes much larger amount of $\text{Ca}(\text{OH})_2$ compared with that consumed by 15% fly ash. Low-calcium ash (FM) consumed larger amount of lime compared with that consumed by the high-calcium ash (OK). However, the moderate-calcium ash C1 consumed the same amount of $\text{Ca}(\text{OH})_2$ as that consumed by the low-calcium ash FM after 6 months which suggests that lower calcium (or higher silica) of the ash does not

necessarily result in higher Ca(OH)_2 consumption. Other parameters (e.g. fineness and amorphous silica content) are known to influence the consumption of Ca(OH)_2 .

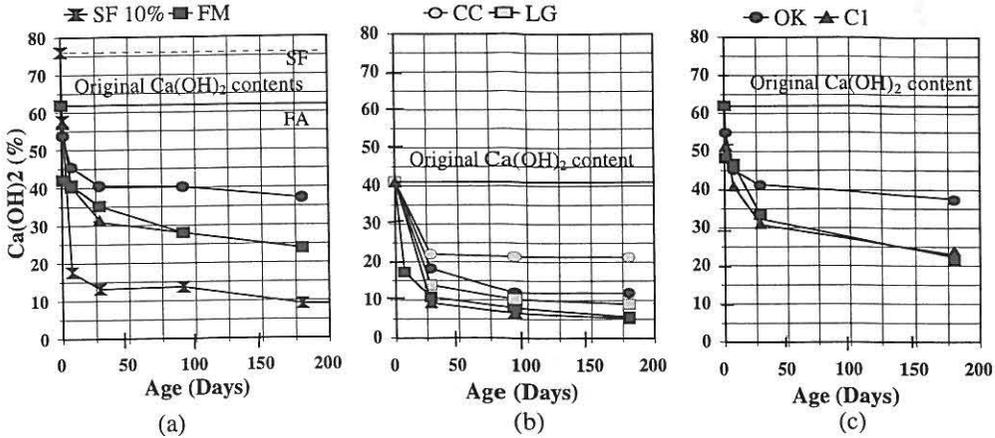


Fig. 2: Effect of pozzolan on Ca(OH)_2 depletion of lime mixes representing: (a) pastes containing 10% SF and 15% FA in high-alkali system, (b) pastes containing 25% FA in high-alkali system, (c) pastes containing 15% FA in low-alkali system.

Figure 2-b shows the consumption of Ca(OH)_2 with 25% fly ash. Except for the CC ash, the unconsumed amounts of Ca(OH)_2 after 3 to 6 months curing were relatively low (i.e. 5% to 12%). The high-calcium ashes CC and OK consumed less Ca(OH)_2 than low and moderate-calcium ashes. Figure 2-c shows the consumption of Ca(OH)_2 in samples representing pastes containing 15% fly ash in low-alkalinity system. It is interesting to note that the Ca(OH)_2 consumed by 15% ash is the same regardless of the alkalinity of the mixing water. The Ca(OH)_2 consumption in the mix representing pastes containing 15% of the ashes FM, C1 and OK in high-alkalinity system after 28 days are 0.27, 0.31 and 0.22, respectively. The corresponding values in low-alkalinity system are 0.29, 0.31 and 0.21, respectively. Similar observations were found at the age of 6 months. Despite similar Ca(OH)_2 consumption which indicates similar pozzolanic reactivity, the ash FM contributed alkalis to the low-alkalinity mixing water and removed alkalis from the high-alkalinity one. This shows that the amount of alkalis that can be bound by the pozzolanic product of hydration increases as the alkali content of the surrounding medium (pore solution) increases; or in other words, as the Na_2O_e of the PC with which the ash is incorporated increases.

Another interesting observation is that the amount of consumed Ca(OH)_2 was found to be dependant on its availability in the system. In the mixes representing pastes containing 15% and 25% fly ash, the initial Ca(OH)_2 contents (as a percentage of ignited mass of the solids at 1050 °C) were 62% and 41%, respectively. The determined Ca(OH)_2 consumption per unit mass of the fly ash was higher in the mixes representing pastes with 15% ash where more Ca(OH)_2 was available in the system. Indeed, the Ca(OH)_2 consumption per unit mass of the ash FM and C1 after 6 months was 0.72 and 0.51 in the 15% and 25% mixes, respectively. Similarly, the amounts of Ca(OH)_2 consumed by OK ash were 0.47 and 0.42 in the 15% and 25% mixes.

Powder X-Ray Diffraction

The X-ray diffractograms of the silica fume, a low-calcium ash (FM) and a high-calcium ash (OK) are shown in Figure 3. The diffraction patterns of the silica fume shows that the sample is composed almost entirely of glass. No evidence of crystalline silica was detected. The glass in the silica fume showed a diffraction halo centred at $2\theta \approx 22^\circ$ indicating that the glass is composed of silica (Diamond 1983; Hemmings and Berry 1988). On the other hand, the diffraction patterns of the fly ashes show crystalline forms of silica (quartz and mullite) indicating that not all the silica in the ash is in the glass phase. Moreover, the centre of the diffraction halo of the glass is shifted to higher 2θ as the calcium content of the ash increases ($2\theta \approx 23-24^\circ$ for FM and $2\theta \approx 32-33^\circ$ for OK). This is attributable to the presence of CaO in the glass phase of the high-calcium ash as reported by Diamond (1983) and Hemmings and Berry (1988).

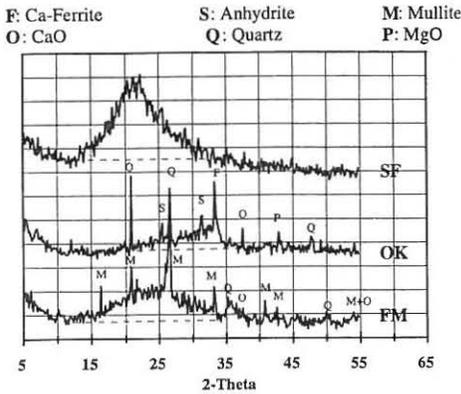


Fig. 3: Powder XRD of the silica fume and FM and OK ashes

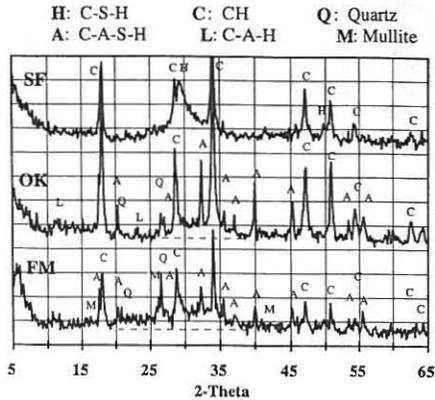


Fig. 4: Powder XRD of the lime mixes after three months curing at 38°C .

The diffraction patterns of the lime/25% FA and lime/10% SF after three months hydration at 38°C are shown in Figure 4. The diffraction patterns of 10% SF/lime mix showed strong peaks of C-S-H indicating the formation of large amounts of this hydrate while other forms of hydrates were not detected. Contrary to the case of the SF sample, the peaks of C-S-H was not easy to detect in the diffraction patterns of the FA/lime mixes. This is partly attributable to the presence of a relatively large number of peaks compared with those found in the SF sample; some of these peaks overlapped with those of the C-S-H. However, the presence of C-A-S-H was clearly detected in both FM/lime and OK/lime mixes.

SEM Examination

Microscopic examination of the samples containing the low and high-calcium ashes (FM and OK, respectively) showed the presence of silica gel in both samples, Figures 5 and 6. However, the composition of the gels in the FM/lime sample was significantly different than that of the gels found in the OK/lime sample. Those formed within the FM sample were low in calcium and high in alkalis ($\text{Ca/Si} \approx 0.13$ and $\text{K+Na} \approx 10\%$, expressed as atomic percent) while those formed with OK were higher in calcium and lower in alkalis

(Ca/Si \approx 0.67 and K+Na \approx 2.1%). C-A-S-H was found in both samples; however, its structure and alkali content were not the same. The C-A-S-H formed within the FM sample was of a fibrous structure with a relatively high potassium content. Figure 7 shows the C-A-S-H forming around FM particle; this type of hydrate (of similar structure and composition) was also found within the bulk sample not in direct association with fly ash particles. On the other hand, the C-A-S-H formed around the OK particle and as outer hydrates were generally featureless and of lower alkali content.

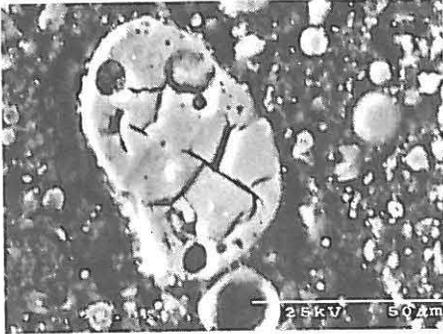


Fig. 5: BSE image showing low-calcium gel forming within the FM/lime mix - 6 months at 38 °C

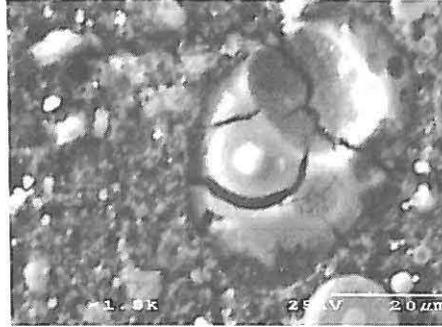


Fig. 6: BSE image showing high-calcium gel forming within the OK/lime mix - 6 months at 38 °C

DISCUSSION

The findings of this paper illustrate the important role of the pozzolanic product of hydration in determining the alkalinity of the pore solution. Within the range of samples investigated, the products of hydration of high-calcium ash were less effective in lowering the pore solution alkalinity than those of low-calcium ash. To further illustrate this observation, the alkalis bound in the products of hydration of the different fly ashes are calculated (for ashes used at 25% in high-alkalinity system). The calculations are performed by subtracting the alkalis in the pore solution from the total alkalis in the system (alkalis added to the mixing water + those from the ash). The available alkali content of the ash (as per ASTM C311) is considered as the alkalis contributed by the fly ash to the system. The amounts of alkalis in the hydration products, expressed as % Na₂O_e of the ash mass, are represented in Figure 8 for the different ashes. As shown in the graph there is a trend of increase in the amount of the bound alkalis as the CaO/SiO₂ of the ash decreases. This explains the higher efficiency of the low-calcium ash in lowering the pore solution alkalinity. The ash LG showed higher bound alkalis compared with FM despite their similar CaO/SiO₂ ratio. This could be a result of the higher Na₂O_e or available Na₂O_e of the LG, which resulted in more alkalis available to the pore solution from the ash. The bound alkalis in the hydrates of this sample could have been increased due to the higher alkalis in the surrounding solution. However, such a high amount of bound alkalis was not large enough to reduce the pore solution alkalinity to a level lower than that of the sample containing fly ash of similar CaO and SiO₂ contents but of lower Na₂O_e content. Duchesne and Berube (1995) also reported an increase in the bound alkalis in the hydrates of high-alkali fly ash.

SEM examination showed a difference in the nature of the reaction products of low and high-calcium ashes with lime. While silica gel and C-A-S-H were detected in both samples containing similar levels of FM and OK; the gel in the FM was of lower Ca^{++} and higher alkali content. The C-A-S-H in the FM was of fibrous structure with higher alkali content than the featureless C-A-S-H found in the OK. The structure and composition of the C-A-S-H requires further investigation.

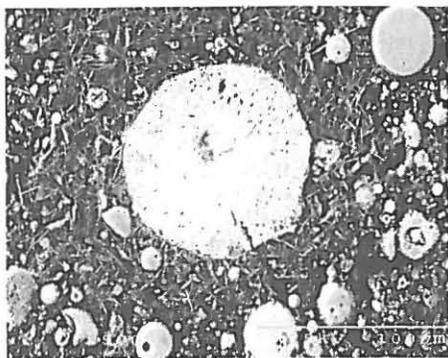


Fig. 7: BSE image showing FM particle with a fibrous C-A-S-H around it.

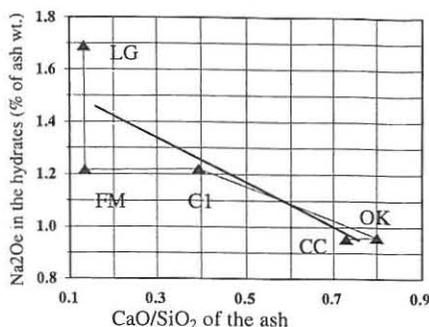


Fig. 8: Effect of CaO/SiO_2 of the ash on the alkalis bound in the hydration

The study also provides an insight into the nature of the pozzolanic reaction of fly ash and the factors affecting its composition. Comparing the amount of Ca(OH)_2 consumed by unit mass of the ash in mixes representing pastes containing 15% and 25% fly ash showed that the Ca(OH)_2 consumption, or Ca^{++} in the product of hydration, was higher in the mixes with lower ash content where more Ca(OH)_2 was available in the system. This illustrates that the composition of the pozzolanic product is not only related to the original composition of the ash, but also to the availability of Ca(OH)_2 in the system.

It should be born in mind that while this study provides an examination of the pozzolanic reaction of fly ash and silica fume without the interference of Portland cement, the products of hydration might not be of the exact composition or behaviour as those produced in Portland cement systems. In the lime mixes investigated in this study, the pozzolans have a better accessibility to Ca(OH)_2 and to the alkaline solution. This is partly because of the high W/CM ratio and partly because of the high availability of Ca(OH)_2 and hydroxyl ions OH^- at the very early age of the mixes (from the time of mixing). While the effect of fly ash on the alkalinity of pore solution of paste samples containing PC/fly ash could be explained based on the alkalis bound by the hydration products of the ash (in the lime mixes), the silica fume showed a performance, in the lime mixes, that is different from that when used with Portland cement. When used with Portland cement, the silica fume showed a considerable reduction in the pore solution alkalinity at early age (28 days) followed by a gradual and significant increase in the pore solution alkalinity thereafter (Shehata and Thomas 2000). In the lime mixes, the silica fume showed the same behaviour at ages up to 28 days (significant reduction in pore solution alkalinity). However, at ages between 28 days and 1 year, the pore solution alkalinity remained unchanged except for a small increase in the alkalinity between 28 and 90 days. Long term performance of the SF/Lime mixes is still under investigation at the University of Toronto.

CONCLUSIONS

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

- Silica fume was found more effective in reducing the pore solution alkalinity and $\text{Ca}(\text{OH})_2$ content than fly ash. Powder XRD showed the formation of C-S-H as the only detected pozzolanic product of hydration of SF with $\text{Ca}(\text{OH})_2$ while C-A-S-H was detected in both mixes containing the low and high-calcium ashes FM and OK.
- For ashes of similar alkali contents, the amount of alkalis bound in the pozzolanic product of hydration increases as the CaO/SiO_2 ratio of the ash decreases.
- The efficiency of fly ash in reducing the pore solution alkalinity of Portland cement/pozzolan pastes can be ascribed to the alkalis bound in the products of hydration of the ash.
- The alkalis bound in the hydration products of a fly ash are higher when the ash is used with high-alkali cement than those bound in the same hydration products when the ash is used with low-alkali cement.
- The calcium consumed by fly ash increases as the calcium availability in the system increases.

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