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Alkali release characteristics of blended cements

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Abstract

This paper presents results of an experimental program conducted to investigate the capacity of hydration products of different cementing materials to retain "bound" alkalis when the alkalinity of the surrounding solution drops. The study covered paste samples containing high-alkali Portland cement and various levels of silica fume and/or fly ash. The results showed that the ability of the hydration products of cement-fly ash systems to bind alkalis is a function of the CaO content of the fly ash, the binding increasing as the calcium content decreases. High-alkali fly ashes ($Na_2O_e > 5.0\%$ and CaO in the range of 15% to 20%) showed considerable amounts of alkali contributed to the test solutions. Silica fume does not have a high capacity to retain alkalis in its hydration products; however, ternary blends containing silica fume and fly ash have excellent capacity to bind and retain alkalis.

Keywords: Alkalis; Alkali–aggregate reaction; Hydration products; Fly ash; Silica fume

1. Introduction

Since the first paper on alkali–silica reaction (ASR) was published in 1940 [1], a great deal of research effort has been directed to understand the mechanism of this deterioration process [2–4] and to develop appropriate preventive measures [5–10]. Research has shown that the use of adequate level of supplementary cementing materials (SCMs) is an effective and feasible way to minimize the risk of deleterious expansion due to ASR [5–10]. The efficacy of SCMs is strongly linked to their ability to lower the level of alkalinity of the concrete pore solution [7,11,12]. It has been claimed that the hydration products of systems containing Portland cement (PC) and SCM have relatively low Ca/Si atomic ratio and this enhances the ability of the hydration products to bind alkalis and hence reduce their availability in the pore solution [13,14]. This high alkali-binding capacity of hydrates of low Ca/Si ratio has been attributed to the hydrate's surface charge. As the Ca/Si decreases, the surface charge becomes less positive, or more negative, and attracts the alkali cations (Na^+ and K^+) from the surrounding pore solution [15].

Supplementary cementing materials contain a certain amount of alkali themselves and, particularly for fly ash, the amount of alkali may exceed that present in Portland cement. For example, chemical analyses collected for fly ashes from over 100 sources in North America showed that the alkali content ranged from less than 1.0% to almost 10%, with an average value of 2.44% sodium oxide equivalent (Na_2O_e). Some of this alkali may be tied up in crystalline products and thus not available for reaction with aggregates. Clearly, it is of interest to determine how much alkali is available from a particular SCM. This is the purpose of the available alkali test in ASTM C 311. Briefly, this test involves mixing 5 g of a pozzolan (such as fly ash) with 2 g of hydrated lime and 10 mL of water and storing the mixture in a sealed container at 38 °C for 28 days. After 28 days, the hardened samples are ground with a small amount of water forming a slurry that is then leached in 200 mL of water for 1 h. Thereafter, the sample is filtered, the residue is washed with hot water (8 to 10 times), and the sodium and potassium concentrations of the filtrate are determined. The problem with this test is that the leaching medium is essentially of neutral pH–i.e. distilled water–and the alkalis available under such test

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conditions do not necessarily represent those that are available in the conditions that prevail in concrete. Indeed, a number of workers [16–19] have shown that most of the alkalis in fly ash or slag will become available under these conditions when the period of curing is extended.

If a blend of SCM and Portland cement is mixed with water and stored under sealed conditions, the alkalis from the Portland cement will be released relatively quickly and those from the SCM will be released over a longer period of time depending on the reactivity of the SCM. As the system approaches full hydration, most of the alkalis will be released (except those in non-reactive crystalline phases) and will be partitioned between the solid (hydrates) and liquid (pore solution) phases of the concrete. The alkali concentration in the pore solution has been shown to be reliably correlated with the alkali, calcium and silica content of the blend of cementing materials; Thomas and Shehata [12] have shown that the OH^- (or $Na^+ + K^+$) concentration of the pore solution is directly related to the parameter $(Na_2O_e \cdot CaO)/(SiO_2)^2$ determined from the chemical composition of the blend. The Na_2O_e represents the total amount of alkali available to the system whereas the silica to calcium ratio represents the binding ability of the hydrates. If the alkali concentration of the pore solution drops, then alkalis will be released from the hydrates to maintain equilibrium between the liquid and solid phases. Other workers [20] have shown that the amount of alkali released is a function of the hydrate composition (Ca/Si) and alkali concentration of the solution. If the hardened cement paste is immersed in water maintained at a neutral pH, most, if not all, of the alkalis in the hydrates will eventually be released.

If a reactive aggregate is introduced into the system, it will react with the alkalis in the pore solution and thus depress the pH of the pore solution. Consequently, alkalis will be released from the hydrates to maintain equilibrium. However, a certain pH is required to sustain the alkali–silica reaction. Diamond et al. [21] showed that the hydroxyl ion concentration of the pore solution of mortars produced with reactive opal decreased with time, reaching a limiting value of 0.28 mol/L. Kollek et al. [22] showed that deleterious expansion in mortar bars containing Beltane opal is unlikely to occur if the OH^- concentration of the pore fluid is less than 0.30 mol/L. Similar behaviour has been observed by Thomas [8] in concretes containing reactive flint aggregate. In this case, the alkali (Na + K) ion concentration of the pore solution reduced slowly over the first 12 months reaching a value of 0.25 mol/L, which remained unchanged at 2 years. The authors of this paper have also shown that mortar bars containing reactive aggregate and tested according to ASTM C 1260 will only expand, at 14 days, if the concentration of the test solution is 0.23 mol/L or higher [23]. Consequently, one could argue that the alkalis that are available for ASR are those that are released from the hydrated system into a solution maintained at an alkali concentration in the range of 0.25 mol/L.

This study was aimed at investigating the amounts of alkali that can be leached from mature paste samples into solutions of different alkalinity. Samples containing binary blends of Portland cement and fly ash or silica fume and ternary blends containing Portland cement, fly ash and silica fume were used. The objective of the experimental program was to evaluate the total amount of alkalis that can be available to solutions of various alkalinity levels with emphasis on a solution of alkali concentration of 0.25 mol/L.

2. Materials and experimental program

The materials used in this study were 12 different fly ashes (FA) having a wide range of chemical composition, one silica

Table 1
Chemical composition and fineness of the cementitious materials (mass%)

ID	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	#325 [c]
Portland cement														
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	1.02	0.24	0.05	–	0.92	–
Silica fume														
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	–
Fly ash														
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	17.80
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	20.80
SD	54.22	21.97	3.95	12.39	1.12	0.21	0.29	2.73	2.92	0.66	0.13	–	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	14.14
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	13.93
BD	41.30	17.35	8.06	18.37	4.22	1.02	0.76	4.85	5.35	0.60	0.3	–	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	12.24
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	14.31
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	18.43
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	15.14
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	10.42
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	23.75

[a] Total alkali ($Na_2O + 0.658K_2O$).

[b] Available alkali, expressed as Na_2O_e, as per ASTM C311.

[c] Fineness determined as material finer than sieve #325.

fume (SF) of high silica and low alkali content, and two Portland cements of high alkali content. The chemical composition of the materials and their fineness values expressed as material retained on a 45-µm sieve (#325) by wet sieving are listed in Table 1. The fly ashes were selected to provide a range of calcium and alkali contents representative of commercially available fly ashes in North America.

Paste samples were cast using various blends of cementing materials at a W/CM ratio of 0.50. The pastes include a control sample that was prepared using high-alkali Portland cement (HAPC 2) as the only cementing material, binary blends containing Portland cement and fly ash or silica fume and ternary blends containing Portland cement, fly ash and silica fume. The various levels and types of SCM blends investigated in this study are listed in Table 2. The high-alkali Portland cement, HAPC 1, was used with pastes containing fly ash, while HAPC 2 was used with pastes containing silica fume and ternary blends of silica fume/fly ash. Samples were mixed using a high-speed, high-shear food blender; the sequence of mixing was 1 min of mixing followed by a 1-min rest period. These mixing and rest periods were repeated twice for a total mixing time of 3 min interrupted by two rest periods of 1 min each. After casting, the samples were sealed in 50-mm diameter × 100-mm height polyethylene cylinders and rotated (normal to their axes) at a speed of 12 rpm for the first 24 h after casting to minimize segregation. The sealed samples were then stored over water at laboratory temperature (23 ± 2 °C) for various curing periods as shown in Table 2.

At the end of the curing period, the paste samples were demoulded and broken into fragments (5–20 mm). Some of the fragments were used for pore solution extractions and the results are reported elsewhere [11,24]. Other fragments were used to determine the evaporable and non-evaporable (bound) water contents by heating the sample, until constant mass, at 105 °C (evaporable water) and 1050 °C (bound water). The determined bound water contents were corrected for loss on ignition (LOI) of the cementing materials. The remaining fragments were stored in a CO_2-free environment (desiccator under vacuum with silica gel and soda lime) until conducting the leaching test.

At the time of running the leaching test, the stored fragments were taken out, crushed and screened to a size of 0.18 mm to 1.25 mm. The moisture content of a sub-sample was determined at the time of immersing the sample into the testing solutions. From the crushed sample, 1.5 g was immersed in 15-ml solution of predetermined alkalinity. The samples and solutions were sealed in polyethylene bottles of 20-mL capacity and stored at room temperature (23 ± 2 °C) for 3 months. The mass of each bottle, after sealing with wax, was determined. A sample of each test solution was also sealed in a container, weighed and stored with the samples to be used as a reference. The control, silica fume, ternary blends, samples containing 25% of the fly ashes labelled FM and OK were tested at solutions of nominal OH^- or $(Na^+ + K^+)$ concentrations of 0.00, 0.10, 0.25 and 0.40 mol/L, while the other samples were tested at solutions of 0.00 and 0.25 mol/L. To obtain statistically representative results, three containers (specimens) were prepared from each sample and tested at each testing solution except for some fly ash samples tested in distilled water where only one container was tested. The solutions were prepared at the same Na_2O to K_2O ratios as those in the cementing materials (PC + SCMs) of the sample being tested. Sodium and potassium ion concentrations were determined by flame photometry. After 3 months, the sealed bottles were reweighed and the leaching solutions were sampled and tested for Na^+ and K^+ ion concentrations. The initial and final masses of the sealed containers were compared to check for evaporation during the 3-month storage period. The changes in the composition of the leaching solutions, after the testing period, were used to determine the amounts of alkali removed from or contributed to the leaching solutions by the samples. Previous preliminary testing conducted by the authors (unpublished) established that a 3-month period was sufficient to allow the system to reach equilibrium (as determined by no further changes in the composition of the solution).

In this paper, the term contributed or available alkalis refers to the amount of alkalis released from the sample into the leaching solution. The alkalis contributed or bound by the samples are calculated and expressed as % Na_2O_e of the original mass of binder or cementing materials (CM) in the samples or as % of total alkalis in the CM. The mass of CM is calculated by subtracting from the total mass of the sample the measured evaporable and chemically bound water at the time of testing and applying a correction to count for loss on ignition of the cementing materials (PC, SF and FA). The concentrations of alkalis in the leaching solutions were also corrected for the pore fluid contributed by the sample (the samples were not completely free from evaporable water when tested).

Table 2
Composition of the tested paste samples

SCM	Level (%)	Age at time of testing (years)	No. of testing solutions*	SCM	Level	Age at time of testing (years)	No. of testing solutions*
LG	25	2	4	OK	25%	3	4
FM	25	3	4	OK	50%	3	2
FM	50	3	2	CC	25%	2	2
BD	25	3	4	HAPC 2		1	4
BD	50	3	2	SF	5%	1	4
SD	25	3	2	SF	10%	1	4
TB	25	2	2	SF/FM	5/10	1	4
C1	25	2	2	SF/FM	5/15	1	4
BR	25	2	2	SF/OK	5/20	1	4
PI	25	2	2	SF/OK	5/30	1	4
C2	25	2	2	SF/OK	10/20	1	4
EW	25	3	2	SF/EW	5/25	1	4

*2: solutions of OH^- concentrations of 0.00 and 0.25 mol/L.
*4: solutions of OH^- concentrations of 0.00, 0.10, 0.25 and 0.40 mol/L.

3. Results and analysis

After the 3-month storage period, the changes in the mass of the sealed bottles were determined and found to be in the range of 0.0007 to 0.0100 g (i.e. about 0.005% to 0.070% of the host solution mass), which indicated that no significant evaporation had occurred during sample storage. The changes in the alkalinity of the leaching solution after 3 months immersion were then assumed to be due to alkalis contributed to or removed from the solution by the sample. In all the cases, except some ternary blend samples tested at solution of 0.40 mol OH^-/L, an increase in the alkalinity of the leaching solution was recorded. This increase represents the total alkalis contributed to the testing solution. Table 3 lists the average and standard deviation values of the contributed alkalis for all the tested samples, expressed as % Na_2O_e per mass of binder or cementing materials.

3.1. Alkalis contributed from the control and binary blend samples

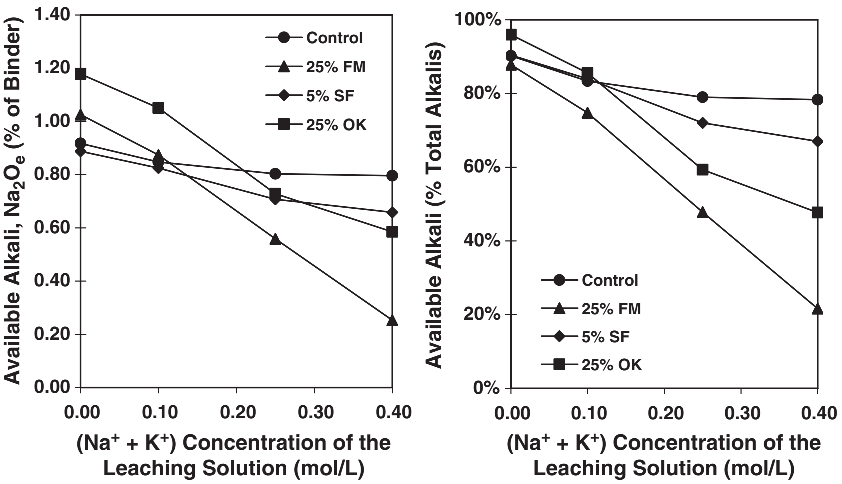
Fig. 1 shows the alkalis contributed from the control and selected binary blend samples to the four leaching solutions. The contributed alkalis are expressed as percentage of Na_2O_e per mass of cementing materials (Fig. 1a) and as a percentage of the original Na_2O_e content of the cementing materials (Fig. 1b). The graphs show that, for the control sample containing only PC, more than 90% of the original alkalis in the PC was released to distilled water. The amount of contributed alkalis reduces as the concentration of alkalis in the leaching solution increases; however, the difference was small. In the leaching solution of 0.40 mol OH^- or $(Na^+ + K^+)$/L, about 80% of the original alkalis were available to the leaching solution.

The samples containing fly ash released more alkalis, than the control, to the distilled water and this is because the original alkali content of these samples are higher than that of the control and the one with SF. Indeed, the data in Fig. 1 show that more than 90% of the alkali of all the tested samples was released to the distilled water. However, at leaching solutions of higher alkalinity especially 0.25 and 0.40 mol/L, the contributed alkalis from the sample containing the low-calcium

Table 3
Average and standard deviation values of the contributed alkalis for all tested samples in different leaching solutions

Sample	Alkalis in test solution (mol/L)	Na_2O_e in raw binder	Contributed Na_2O_e as % of binder mass	
			Average	S.D.
Control	0	1.017	0.920	0.002
	0.1	1.017	0.848	0.012
	0.25	1.017	0.803	0.029
	0.4	1.017	0.796	0.080
25% FM	0	1.168	1.026	0.024
	0.1	1.168	0.874	0.006
	0.25	1.168	0.559	0.011
	0.4	1.168	0.253	0.037
25% OK	0	1.228	1.178	0.004
	0.1	1.228	1.050	0.007
	0.25	1.228	0.728	0.020
	0.4	1.228	0.585	0.263
25% BD	0	2.153	1.752	
	0.25	2.153	1.470	0.033
25% SD	0	1.546	1.340	
	0.25	1.546	0.777	0.012
25% EW	0	1.236	1.170	
	0.25	1.236	0.756	0.009
50% FM	0	1.249	0.873	
	0.25	1.249	0.333	0.228
50% OK	0	1.368	1.319	
	0.25	1.368	0.619	0.019
BD 50%	0	3.219	2.175	
	0.25	3.219	1.835	0.160
25% CC	0	1.380	1.128	
	0.25	1.380	0.740	0.104
25% PI	0	1.578	1.114	
	0.25	1.578	0.563	0.030
25% C1	0	1.236	1.145	
	0.25	1.236	0.640	0.012
25% C2	0	1.302	1.208	
	0.25	1.302	0.711	0.020
25% LG	0	1.390	1.210	
	0.25	1.390	0.684	0.033
25% BR	0	2.998	2.663	
	0.25	2.998	2.237	0.022
25% TB	0	2.931	2.565	
	0.25	2.931	2.127	0.074
5% SF	0	0.982	0.888	0.008
	0.1	0.982	0.825	0.005
	0.25	0.982	0.707	0.034
	0.4	0.982	0.658	0.043
10% SF	0	0.947	0.835	0.000
	0.1	0.947	0.786	0.008
	0.25	0.947	0.683	0.048
	0.4	0.947	0.606	0.036
SF/FM 5/10	0	1.021	0.889	0.002
	0.1	1.021	0.665	0.045
	0.25	1.021	0.397	0.015
	0.4	1.021	0.240	0.108
SF/FM 5/15	0	1.041	0.884	0.002
	0.1	1.041	0.556	0.010
	0.25	1.041	0.150	0.013
	0.4	1.041	−0.075	0.086
SF/OK 5/20	0	1.108	1.018	
	0.1	1.108	0.765	0.010
	0.25	1.108	0.331	0.018
	0.4	1.108	−0.335	0.152
SF/OK 5/30	0	1.171	1.046	0.002
	0.1	1.171	0.805	0.063
	0.25	1.171	0.246	0.085
	0.4	1.171	−0.673	0.074
SF/OK 10/20	0	1.073	0.925	0.004
	0.1	1.073	0.584	0.018
	0.25	1.073	0.063	0.021
	0.4	1.073	−0.131	0.016
SF/EW 5/25	0	1.148	1.027	0.008
	0.1	1.148	0.769	0.017
	0.25	1.148	0.344	0.010
	0.4	1.148	−0.126	0.129

Samples with no standard deviations are those where only one specimen was tested.



(a) (b)

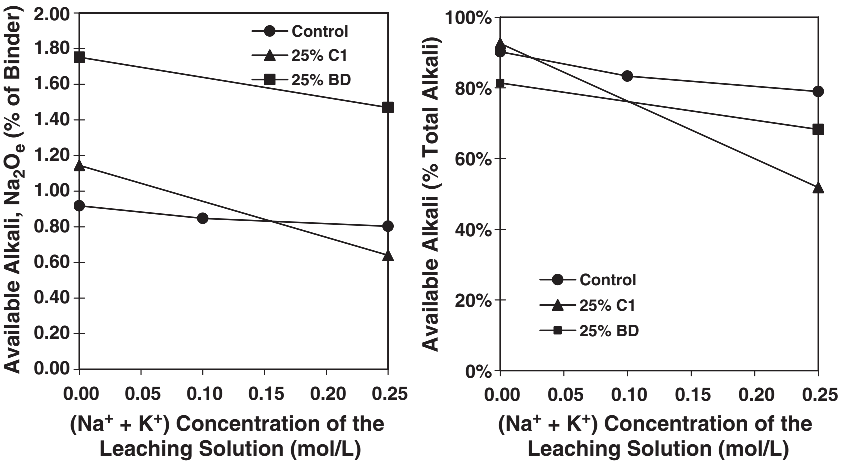
Fig. 1. Available alkalis from control and binary blends in leaching solutions of different alkali concentrations: (a) expressed as % of mass of binder or cementing materials and (b) expressed as % of the total alkali content of the binder.

fly ash FM was significantly lower than that contributed by the control, SF and the OK (high-calcium fly ash) samples. This indicates that the hydration products of the PC/FM sample have a higher capacity to retain alkalis compared to the other three samples. Indeed, the amount of alkalis retained by the hydration products of this sample when immersed in solution of 0.25 mol/L of OH^- is 53% of the total alkali content of the blend. The amount of alkalis retained by the PC, 5% SF and 25% OK samples when leached in a solution of the same alkalinity are approximately 20%, 25% and 40%, respectively. The ability of the cementing system to bind and retain alkalis in its hydration products reflects their ability to reduce expansion due to ASR. Indeed, parallel studies [7] showed that the FM ash was effective in maintaining the 2-year expansion of concrete prisms below 0.04% while the HAPC 2, 5% SF and 30% OK achieved 2-year expansion values of 0.25%, 0.21% and 0.14%, respectively.

3.2. Effect of fly ash composition and level of replacement

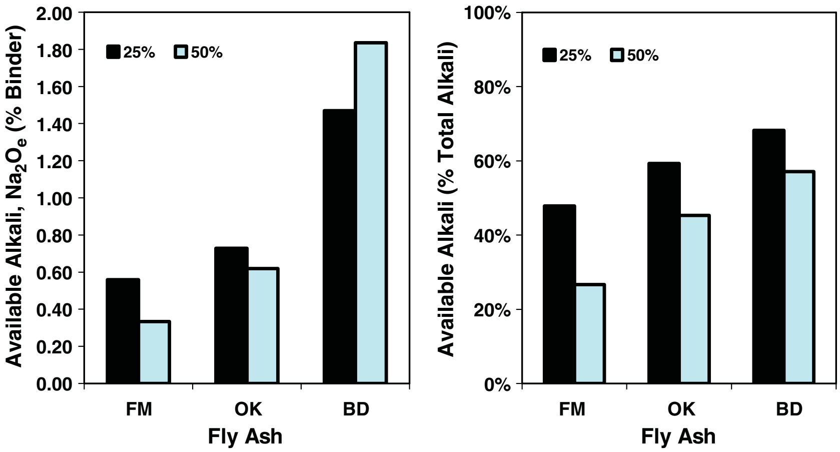
The efficiency of fly ash to bind and retain alkalis was found to be related to the chemical compositions of the ash, mainly its calcium and alkali oxides. This is also illustrated in Fig. 1, which compares the performance of two fly ashes, FM and OK, of similar alkali contents (1.41% and 1.75% Na_2O_e, respectively) but different CaO contents (6.38% and 27.71%, respectively). For leaching solutions of 0.25 and 0.40 mol/L, both fly ashes performed better than the control sample. However, the alkalis contributed by the low-calcium fly ash FM was lower than that contributed by the high calcium ash OK.

The effect of alkali content of the fly ashes is illustrated in Fig. 2. In this figure, the results of the two fly ashes C1 and BD are shown. These two fly ashes have similar CaO contents (17.51% and 18.37%, respectively) but different



(a) (b)

Fig. 2. Effect of alkali content of fly ash on available alkalis in leaching solutions of different alkali concentrations: (a) expressed as % of mass of binder or cementing materials and (b) expressed as % of the total alkali content of the binder.



(a) (b)

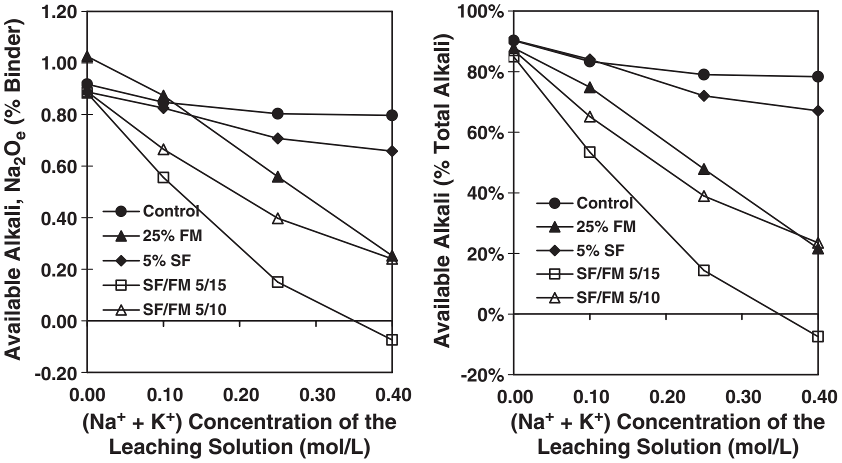
Fig. 3. Effect of fly ash replacement level of alkalis available to a leaching solution of alkali concentration = 0.25 mol/L: (a) expressed as % of mass of binder or cementing materials and (b) expressed as % of the total alkali content of the binder.

alkali contents (1.68% and 5.35%, respectively). As Fig. 2 shows, much more alkalis are contributed from the sample containing the high-alkali fly ash BD. Moreover, the alkalis contributed to the 0.25 mol/L solution by the BD ash expressed as a percentage of the total alkali content of the binder was approximately 70% versus 50% for the C1 ash as the figure shows. This suggests that the alkali content of BD fly ash is much higher than the binding capacity of its hydrates. This is why a large percentage of this fly ash's alkali content is available to the leaching solution and less is retained by its hydrates.

Fig. 3 shows the effect of level of replacement of fly ash on the total contributed alkalis into a solution of 0.25 mol/L. As the figure shows, higher replacement levels of FM and OK fly ashes reduce the total amount of contributed alkalis to the leaching solutions. These two fly ashes have low alkali content (<2.0% Na_2O_e). On the other hand, the sample containing the high alkali fly ash BD showed the opposite trend, the higher the replacement level the larger the amount of alkalis contributed to the leaching solution. When the available alkalis are expressed as percentage of total alkalis, the three fly ashes showed less available alkalis at higher replacement level. Regardless of how the available alkali is expressed, the high-alkali fly ash sample (BD) showed higher contributed alkalis compared to those contributed by the low and high-calcium fly ashes (FM and OK) of low alkali contents.

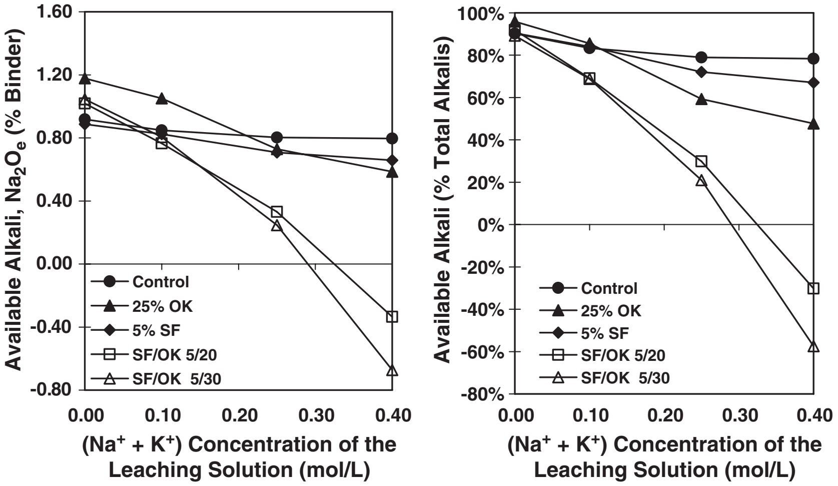
3.3. Alkalis contributed from ternary blend pastes containing PC, FA and SF

The effects of ternary blends containing PC+SF+FA on the availability of alkalis to different leaching solutions are illustrated in Figs. 4–6. Fig. 4 compares the performance of two binary blends containing 5% silica fume and 25% low-calcium fly ash (FM) and that of ternary blends that combine



(a) (b)

Fig. 4. Alkali contribution from pastes containing binary and ternary blends of silica fume and the low-calcium fly ash FM: (a) expressed as % of mass of binder or cementing materials and (b) expressed as % of the total alkali content of the binder.



(a) (b)

Fig. 5. Alkali contribution from pastes containing binary and ternary blends of 5% silica fume and the high-calcium fly ash OK: (a) expressed as % of mass of binder or cementing materials and (b) expressed as % of the total alkali content of the binder.

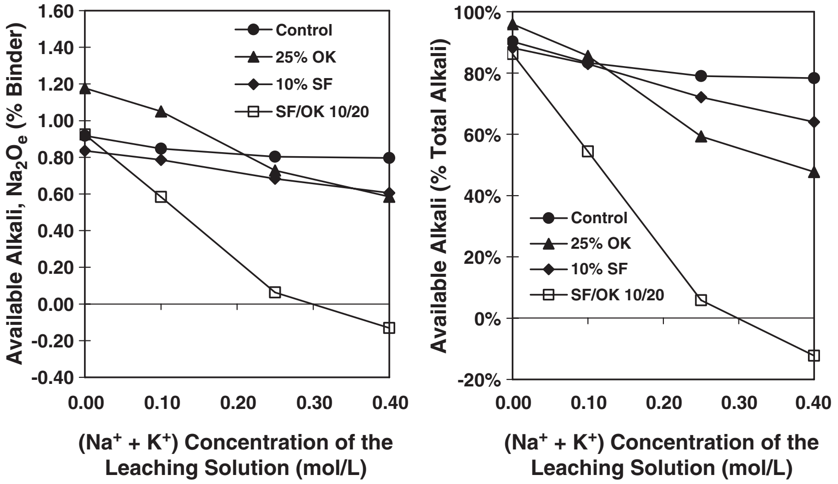
the two materials (in addition to Portland cement). As Fig. 4 shows, significantly less amount of alkalis were available to all tested leaching solutions from blends containing 5% silica fume and 10% or 15% FM compared to alkalis available from 25% FM or 5% silica fume when used in binary blends as the sole SCM.

Similar behaviour was observed for the ternary blends containing SF and the high-calcium fly ash OK. As Fig. 5 shows, the alkalis available from blends containing 5/20 or 5/30 SF/OK were much less than those contributed from the binary samples containing 5% SF or 25% OK.

The positive effect of ternary blends on the availability of alkalis is also illustrated in Fig. 6, which represents the results of samples containing 10% SF and 10/20 SF/OK. Using 10% silica fume did not have significant improvement on the alkalis available to leaching solutions as shown in the Figure. However, when 20% OK was added to the 10% SF, the availability of alkalis was significantly reduced.

3.4. Relationship between composition of binder and "available alkali"

The simple relation shown in Fig. 7 combines the effect of cementing blend composition and replacement level on the total alkalis available to a leaching solution of 0.25 mol/L. A reasonable correlation was found between the parameter ($Na_2O_e \times CaO/SiO_2$) and the available alkalis. Including the alumina content in the parameter did not have a noticeable statistical effect on the relation. The oxide composition of the cementing materials is calculated based on the composition of each material and its percentage in the mix. For instance, the CaO content of a blend containing 25% fly ash is the sum of the 0.75 × CaO of Portland cement and 0.25 × CaO content of the fly



(a) (b)

Fig. 6. Alkali contribution from pastes containing binary and ternary blends of 10% silica fume and the high-calcium fly ash OK: (a) expressed as % of mass of binder or cementing materials and (b) expressed as % of the total alkali content of the binder.

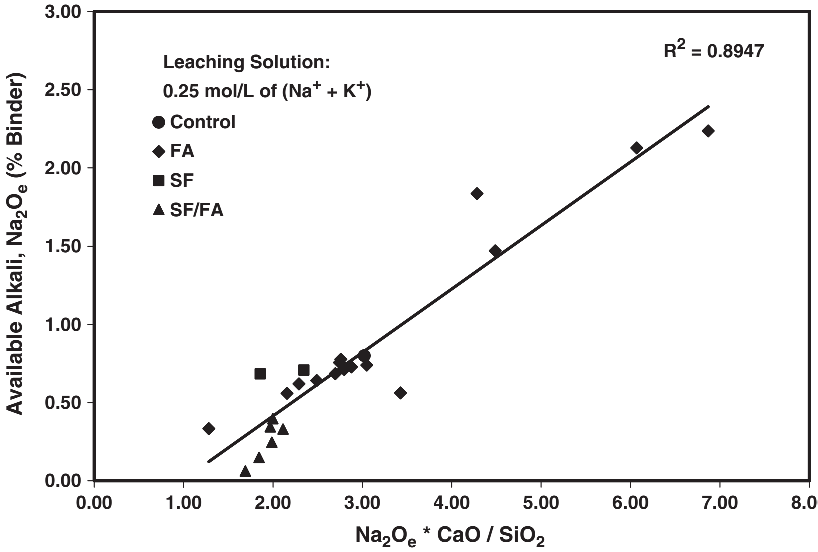


Fig. 7. Effect of chemical compositions of cementing blends on available alkalis in leaching solution of alkali concentration of 0.25 mol/L.

ash. As shown in the graph, the ability of a blend to reduce alkali availability increases as its silica content increases and its alkali and calcium contents decrease.

4. Discussion

The data presented in this paper complements the results of pore solution studies conducted by the authors and other researchers [12,24,25]. The composition of pore solution of mature paste samples reflects a state of equilibrium between the liquid (pore solution) and solid (hydration products) phases in the sample. If such a state of equilibrium is altered, alkalis can move from one phase to the other. The research program presented in this paper was directed to investigate the possibility of alkalis being released from the hydration products of different cementing blends to the pore solution if the alkalinity of the latter drops. This drop can be a result of alkali being consumed by reactive aggregates. The results showed that the ability of a blended cement to bind and retain alkali in its hydration products depends upon the oxide composition of the blend. This was also the case for the ability of the blends to reduce pore solution alkalinity and expansion as reported by the authors in other research works [7,11,12].

The relation between the total alkali available to solution of 0.25 mol/L and expansion of concrete prisms containing the same cementing blends and a reactive siliceous limestone from Ottawa (Spratt) is presented in Fig. 8. The 2-year expansion results shown in the graphs are either measured for samples containing the same level of SCM as those used in the paste samples tested in the alkali leaching test, or estimated by interpolating expansion results where prisms containing the same level of SCM used in the paste samples are not available. The graphs show a level of Na_2O_e (≈ 0.67%

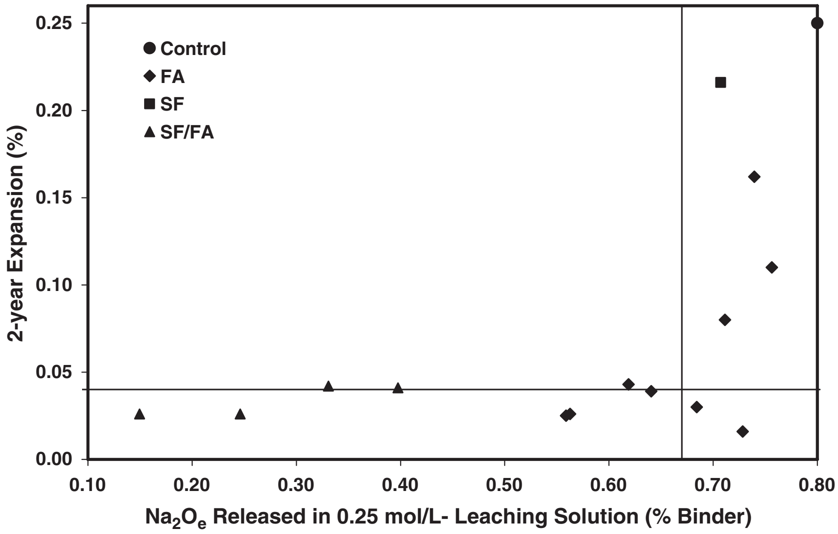


Fig. 8. Two-year expansion versus available alkalis for all tested SCM except fly ashes of $Na_2O_e > 5.0\%$.

of binder mass) available in solution of 0.25 mol/L OH^- concentration after which the expansion of the concrete prisms exceeds 0.04%. Blends that show alkali contribution larger than this limit are the control and those containing binary blends of SF or fly ash of CaO > 20%. Fly ashes of $Na_2O_e > 5.0\%$ (not included in the graph) showed alkali contribution between 2.00% and 2.50%. Despite that, the expansions of concrete containing these fly ashes were less than that of the control, which showed an alkali contribution of 0.80%. This shows that the amount of alkalis available for reaction with reactive aggregates is not the only factor that controls ASR. There are other factors that influence ASR expansion, at least for the reactive aggregate used in this study. It is quite possible that the reduced availability of calcium when SCM is used plays a role as suggested by other research work [26,27]. No clear relation was found between the 2-year expansion and the total alkalis or available alkalis of the fly ash determined by ASTM C311.

It is interesting to note that increasing the level of the high-alkali fly ash BD increases the availability of alkalis in leaching solutions. This was not the case for low-alkali fly ashes regardless of their calcium contents. This is consistent with the composition of pore solution, higher level of this ash showed pore solution of higher alkalinity [24]. This suggests that using larger amounts of high alkali fly ash may not be beneficial in suppressing ASR in the long term. Although the concrete expansion showed lower values when this fly ash was used at higher level with Spratt aggregates, this may not be the case with other types of reactive aggregates.

The data presented in this paper also emphasizes the synergy that exists when SF and FA are used in the same blend. This can be seen clearly in case of the sample containing 5/20 SF/OK. The total Na_2O_e leached in solution of alkali concentration of 0.25 mol/L were 0.80%, 0.71% and 0.73% Na_2O_e for the control, 5% SF and 25% OK, respectively. When 5% silica fume was used with 20% OK, the leached alkali was only 0.33% of mass of cementing materials. The reduction in alkali availability of the SF/OK sample, compared to the control sample, is 0.43% Na_2O_e, while the sum of reductions of the two materials if used individually in binary blends is $0.09 + 0.07 = 0.16\%$. Similar synergistic effects of ternary blends on the pore solution alkalinity and a suggested mechanism of this synergy were presented by the authors in an earlier publication [11].

5. Conclusions

Within the range of materials investigated in this study, the following conclusions are drawn:

1. The alkalis available from PC–SCM systems to surrounding solutions of various alkalinity increase as the calcium and alkali contents of the blends increase and their silica content decreases.
2. The total alkalis contributed from fly ash of CaO > 20% to various leaching solutions were larger than those contributed from ashes of CaO < 20%. The increased alkali contribution is the main reason behind the low efficiency of high-CaO fly ash to mitigate expansion due to ASR.
3. The total alkalis available to various testing solutions for samples containing high-alkali fly ash were much higher than those contributed by fly ashes of lower alkali contents. These fly ashes may be expected to provide a considerable source of alkalis if the alkalinity of pore solution drops due to alkali being consumed by reactive aggregates.
4. Ternary blends containing silica fume and fly ash showed superior performance in terms of binding and retaining alkalis. The performance of high-calcium fly ashes that are not effective in reducing alkali availability can be significantly improved when combined with 5% SF. Silica fume on its own did not show a high capacity to bind or retain alkalis in its hydration products when used at replacement levels of 5% or 10%.
5. The results obtained from this experimental program suggest that the procedure followed here can be optimized and used as a screening tool for evaluating the efficacy of SCM in mitigating ASR especially for SCM which performance cannot be predicted only based on their oxide composition.

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