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Effect of Supplementary Cementing Materials on the Composition of Cement Hydration Products

J. Duchesne* and M.A. Bérubé†
*Department of Earth Sciences, University of Waterloo, Waterloo, Ontario, Canada and
†Département de Géologie et de Génie Géologique, Université Laval, Sainte-Foy,
Québec, Canada

Composition of cement hydration products in concretes made with two condensed silica fumes, three pulverized fly ashes (PFA), and one ground granulated blast furnace slag, and stored at 38°C and 100% relative humidity for 3 years was analyzed using an electron probe microanalyzer. The pore solution expression method was also applied on pastes to analyze the composition of the pore water. The mean CaO/SiO_2 (C/S) mole ratio of hydrates in the ordinary Portland cement (OPC) control concrete was 2.05. In blended concretes, this ratio decreased to between 1.24 and 1.46, however with no clear distinction from one supplementary cementing material (SCM) type to another. All blended pastes except the one with the very alkali-rich PFA tested showed a drop in the alkali concentration of the pore solution compared with the control paste. Mass balance calculations indicated that lower C/S hydrates produced in the presence of SCM can contain much more alkali than OPC hydrates, provided that more alkali is available. These SCMs may decrease the alkalinity and the pH of the pore solution, and reduce expansion due to alkali silica reactivity. ADVANCED CEMENT BASED MATERIALS 1995, 2, 43–52

KEY WORDS: Alkali-silica reactivity, Alkalies, Calcium silicate hydrate, Concrete, Condensed silica fume, Ground granulated blast furnace slag, Pulverized fly ash

Supplementary cementing materials (SCMs) such as condensed silica fume (CSF), pulverized fly ash (PFA), and ground granulated blast furnace slag (GGBFS) find extensive use in concrete technology. Their utilization is one of the most popular methods proposed to suppress concrete expansion due to alkali-silica reactivity. However, their behavior is not completely understood and care must be taken to control alkali-aggregate expansion in this way. According to Bhatty [1], SCMs reduce or eliminate alkali-aggregate expansion by producing additional and low-CaO calcium silicate hydrates (C-S-H). These hydrates can entrap more alkali, thus reducing the amount of alkali ions available in the pore solution for reaction with potentially reactive aggregates.

The composition of cement hydration products was measured by a number of authors and some results appear in Table 1. This composition varies with the SCM type (PFA, CSF, or GGBFS) [2,3], variety (same type) [13], and amount used as cement replacement, as demonstrated by the particularly low CaO/SiO_2 (C/S) mole ratios obtained with 30% CSF [8,10] compared with lower cement replacement levels [3]. For a given SCM type, the C/S mole ratio of hydrates varies considerably in Table 1: from 1.55 to 2.03 (average = 1.82), 1.01 to 1.57 (average = 1.32), 0.8 to 1.43 (average = 1.02), and 0.9 to 1.65 (average = 1.29) for ordinary Portland cement (OPC) (control), PFA, CSF, and GGBFS blended mixtures, respectively.

The C/S mole ratio is clearly greater for OPC controls than for OPC + SCM mixtures. However, just a few investigations involved different types of SCM and/or different varieties of the same SCM type. Concerning the alkali contents of hydrates, all studies listed in Table 1 except one [3] reported higher alkali contents for SCM blended mixtures compared with OPC controls [8,10].

The objective of this study was to measure the composition of hydrates in cement paste of blended concretes made with various types and varieties of CSF, PFA, and GGBFS. An electron probe microanalyzer (EPMA) was used to determine the composition of hydrates in concrete samples. The pore solution expression method [15] was also used to analyze the composition of pore water in corresponding paste samples.

Experimental Procedures

Materials

Two ordinary type 10 Portland cements (OPC) and six SCMs were used for making concrete and paste spec-

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Address correspondence to: Josée Duchesne, Department of Earth Sciences, University of Waterloo, Waterloo, Ontario, N21 3G1 Canada.
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655 Avenue of the Americas, New York, NY 10010

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TABLE 1. Literature survey of composition of calcium silicate hydrates

C/S	K_2O (%)	Na_2O (%)	Mixture	Remarks	Reference
2.03	0.11	0.03	OPC	EPMA, 4 years, 20°C	Uchikawa [2]
1.01	0.33	0.24	40% PFA		
1.62	0.33	0.23	40% GGBFS		
1.90	0.33	0.33	OPC	EPMA, 2 months, 45°C	Uchikawa et al. [3]
1.43	0.32	0.33	10% CSF		
1.32	0.78	0.25	40% PFA		
1.65	0.28	0.15	40% GGBFS		
1.1 ~ 1.2			PFA	10 years, mortar	Sato and Furuhashi [4]
1.0			CSF	24 hours, 20°C	Roy [5]
0.8 to 1.5			C3S-CSF		Li and Roy [6]
			C3S-CSF		
1.71	0.58		OPC	EPMA, 8 years	Rayment [7]
1.55	0.76		20% PFA		
1.55	0.1		OPC	EPMA	Poitevin and Regourd [8]
0.9	1.1		30% CSF		
1.94	0.15		OPC	EPMA, 7 years, concrete	Thomas et al. [9]
1.57	0.68		20 to 30% PFA		
1.8	0.5		OPC	EPMA	Regourd [10]
0.9	1.3		30% CSF		
~1.1			CSF		Traetteberg [11]
~1			GGBFS	EPMA	Dron et al. [12]
1.0			70% GGBFS	EPMA, 28 days, 20°C	Regourd [13]
0.9			70% GGBFS		
1.3			70% GGBFS		
1.55			30% gr. slag	EPMA	Regourd et al. [14]
1.20			25% gr. slag + 5% CSF		
1.70			30% cr. slag		
1.43			25% cr. slag + 5% CSF		

gr. slag = granulated slag; cr. slag = crystalline slag.

imens. The chemical composition of all materials is given in Table 2. The SCMs consisted of two CSFs, three PFAs, and one GGBFS. The CSFs and PFAs were chosen in order to have different alkali contents and, for the latter, various CaO contents. The crystalline constituents of the SCM are given in Table 3. The aggregate used for making concrete was a very alkali-silica reactive rhyolitic tuff from the Beauceville quarry (Québec, Canada). This aggregate contains large amounts of alkali-reactive microcrystalline quartz.

Sample Preparation

COMPOSITION OF HYDRATES. Concrete prisms were made with 350 kg/m^3 of cementitious materials [OPC (A) + SCM] and a fixed 0.5 water: (OPC + SCM) ratio. The alkali content was raised to 1.25% Na_2O_{eq} of the cement (OPC) mass by adding NaOH to the mixture water. The control was made without any SCM, while 10% CSF, 40% PFA, or 50% GGBFS was used in blended concretes as cement replacement by mass. Concrete specimens were stored at 38°C and 100% relative humidity (RH). After 3 years of curing, polished sections were made from the specimens. The hydrates were thus analyzed by wavelength dispersive X-ray analysis with an EPMA using an accelerating voltage of 20 kV and a specimen current of 0.1 μmA. A ZAF correction of Bence-Albee type was applied on the analysis. A total of 50 analyses were performed for each blended concrete and 75 for the control, with the analysis points random-visually selected.

TABLE 2. Chemical composition of cements and supplementary cementing materials

Oxide	PFA			CSF			Cement	
(%)	A	B	C	A	B	GGBFS	A	B
SiO_2	42.20	53.90	32.59	94.17	74.60	36.60	20.66	20.47
Al_2O_3	21.60	20.90	17.93	0.21	0.59	8.00	4.62	5.51
Fe_2O_3	27.60	3.52	5.94	0.32	6.54	0.67	3.11	2.45
MgO	0.92	1.11	4.12	0.47	1.56	13.70	2.31	2.82
CaO	1.87	12.00	20.70	0.50	0.40	37.20	61.76	63.12
Na_2O	0.66	2.74	8.08	n.d.	1.68	0.44	0.20	0.29
K_2O	2.55	0.50	0.72	1.17	2.97	0.31	0.82	1.16
SO_3	1.10	0.09	1.48	0.12	0.81	3.97	2.98	2.60
LOI	1.85	0.57	0.96	2.77	7.34	n.a.	2.82	0.81
Na_2O_{eq}	2.34	3.07	8.55	0.77	3.63	0.64	0.74	1.05

n.d. = not detected; n.a. = not analyzed.

COMPOSITION OF PORE WATER. Paste samples were made with the same water: (OPC + SCM) ratios and SCM contents as for concrete specimens. Cement B was used for all samples. Pastes were cast into plastic bottles stored at 38°C and 100% RH above water in a sealed container. After 1 year of curing, pore solutions were expressed from hardened cement pastes by the high pressure method [15]. A maximum load pressure of 560 MPa (81,500 psi) was applied to all samples. Shortly after expression, chemical analysis of K^+ and Na^+ ions was carried out on the solutions by atomic absorption.

Results and Discussion

Chemical Composition of Hydrates in Concrete Specimens

Results from the chemical analysis of hydrates present within the concrete specimens are summarized in Table 4. Major oxides CaO, SiO_2, and Al_2O_3 are given together with corresponding CaO/SiO_2 (C/S) and CaO/Al_2O_3 (C/A) mole ratios.

STATISTICAL CONSIDERATIONS. The CaO, SiO_2, and Al_2O_3 contents and the corresponding C/S and C/A mole ratios vary irregularly from point to point as indicated by relatively high standard deviation values in Table 4. According to Taylor [16], most investigators reported considerable scattering between the results of individual analyses performed on polished sections with the EPMA or scanning electron microscopy (SEM). Figure 1 presents the frequency distribution of the C/S mole ratio for each concrete tested. Each set of results shows a unimodal distribution, contrary to measurements by Stuke and Majumdar [17], who found a bimodal distribution for OPC pastes. These results were attributed to different compositions for inner and outer hydration products. According to the χ^2 distribution test applied to the present results, there is no evidence that the C/S ratios are not normally distributed. Indeed, for each concrete, the χ^2 values are lower than the critical value of 3.84 for one degree of freedom and a 5% level of significance. The single distribution of hydration prod-

TABLE 3. Crystalline constituents of SCM

SCM	Diffuse Band (Glass) (θ)	Crystalline Constituent											
		Qzt	Mag	Hem	Mul	Syl	FeSi	Mer	Gyp	Cal	Geh	The	C_3A
CSF-A	12		●			●							
CSF-B	13	●	●	●		●	●						
PFA-A	14	●	●	●	●								
PFA-B	14	●			●								
PFA-C	13 and 18	●	●	●					●	●	●	●	●
GGBFS	18							●					

X-Ray diffraction using CoKα radiation.

Qzt	quartz (SiO_2)	Mag	magnetite (Fe_3O_4)	Hem	hematite (Fe_2O_3)
Mul	mullite ($Al_6Si_2O_{13}$)	Syl	sylvite (KCl)	FeSi	ferro-silicum (Fe_2Si)C
Mer	merwinite ($Ca_3Mg(SiO_4)_2$)	Gyp	gypse ($CaSO_4 \cdot 2H_2O$)	Cal	calcite ($CaCO_3$)
Geh	gehlenite ($Ca_2Al_2SiO_7$)	The	thenardite (Na_2SO_4)	C_3A	($Ca_3Al_2O_6$)

TABLE 4. Microanalysis results of calcium silicate hydrates in concrete samples

Blended Concretes	Concrete Mixture	Statistical Data	Oxide (Weight %)			Mole Ratio		No. of Analyses
			CaO	SiO_2	Al_2O_3	C/S	C/A	
Control	100% OPC	Mean	32.76	17.60	2.92	2.05	22.94	75
		SD	4.64	2.89	1.15	0.46	7.64	
	60% OPC +	Mean	27.04	21.99	6.86	1.35	7.48	50
	40% PFA-A	SD	3.36	3.90	1.59	0.22	1.62	
PFA	60% OPC +	Mean	28.14	21.31	6.41	1.44	8.41	50
	40% PFA-B	SD	3.73	3.11	1.64	0.23	2.04	
	60% OPC +	Mean	26.31	20.29	6.53	1.43	7.87	50
	40% PFA-C	SD	4.14	3.70	1.99	0.29	2.09	
	90% OPC +	Mean	30.08	26.35	4.45	1.24	13.11	50
	10% CSF-A	SD	3.40	3.23	1.33	0.18	3.29	
CSF	90% OPC +	Mean	32.20	24.18	3.88	1.46	16.35	50
	10% CSF-B	SD	3.95	3.97	1.30	0.26	4.45	
GGBFS	50% OPC +	Mean	29.62	23.92	5.75	1.33	10.12	50
	50% GGBFS	SD	3.70	2.96	1.57	0.15	3.26	

ucts is evident at the level of volume sampling (micrometers^3). At higher resolution this might not hold true (e.g., nm^3).

One can note in Table 4 that the standard deviation for CaO is higher for the control than for blended concretes, with the reverse being observed for SiO_2 and Al_2O_3. This could be attributed to the higher amount of portlandite in the control, as discussed elsewhere [18], which may be randomly intermixed with pure C-S-H. As a result, the standard deviations for both C/S and C/A mole ratios are also higher for the control concrete, as shown in Figure 2, which presents these ratios for the control and the concrete made with 40% PFA-B. The above results thus also suggest that at the level of analysis (micrometer scale), for a given OPC-SCM blended concrete, there is only one distribution of hydrates with respect to composition, despite the presence of two very different cementitious materials (OPC and SCM).

CHEMICAL COMPOSITION OF CEMENT HYDRATION PRODUCTS. The average CaO, SiO_2, and Al_2O_3 contents of the initial mixtures of cementitious materials (e.g., OPC + SCM) are shown in Figure 3A. According to the cement replacement used in each case, it can be observed that: (1) the three above oxides always count for about 90% by weight of each initial blend, except for about 80% for blends containing PFA-A, which is Fe_2O_3 rich, and PFA-C, which contains significant amounts of other oxides such as Fe_2O_3, MgO, and Na_2O; (2) all SCMs tested contribute to decrease the CaO content of the cementitious mixture compared with the OPC control; (3) however, they all increase the SiO_2 content; and (4) the Al_2O_3 content was increased with the three PFAs.

The corresponding results for the hydrates produced by each mixture in concrete specimens are shown in Figure 3B. One can observe that the three major oxides count for 53 to 61% by mass of hydrates. One can also observe that the Al_2O_3 and the SiO_2 content of hydrates increased with each SCM used compared with the control. Finally, Figure 3B shows that the CaO content of hydrates is relatively similar to the two CSFs compared with the control; even if only 10% silica fume was used as cement replacement, this result is quite surprising considering that calcium is less than 1% in the two CSFs tested.

C/S AND C/(S + A) MOLE RATIOS IN CEMENT HYDRATION PRODUCTS. The average C/S mole ratios of each initial mixture of (OPC + SCM) and corresponding hydrates produced in concretes are shown in Figure 4A. It can be noted that: (1) the C/S ratio is significantly lower in OPC + SCM mixtures (1.4 to 2.5) than in the cement (3.3), particularly with the two type F fly ashes A and B; (2) the C/S ratio in corresponding hydrates is also significantly lower for each blended concrete (1.24 to 1.46) compared with the control (2.05), with the lowest value being obtained with the high silica CSF-A; (3) however, the C/S mole ratio in hydrates is not very different from one blended concrete to another (excluding the control), in other words, from one type of SCM to another; furthermore, the highest C/S value is obtained with CSF-B (1.46), while the lowest value corresponds to the other silica fume CSF-A (1.24); (4) there is no significant correlation between the C/S mole ratio in hydrates and the same ratio in the initial cementitious mixture, which was to be expected considering that some silica of SCM is in unreactive crystalline phases (quartz, mullite, etc.); (5) the CaO/(SiO_2 + Al_2O_3) or C/(S + A) mole ratio (not illustrated) shows exactly the same trends as the C/S mole ratio, both for hydrates and initial cementitious mixtures.

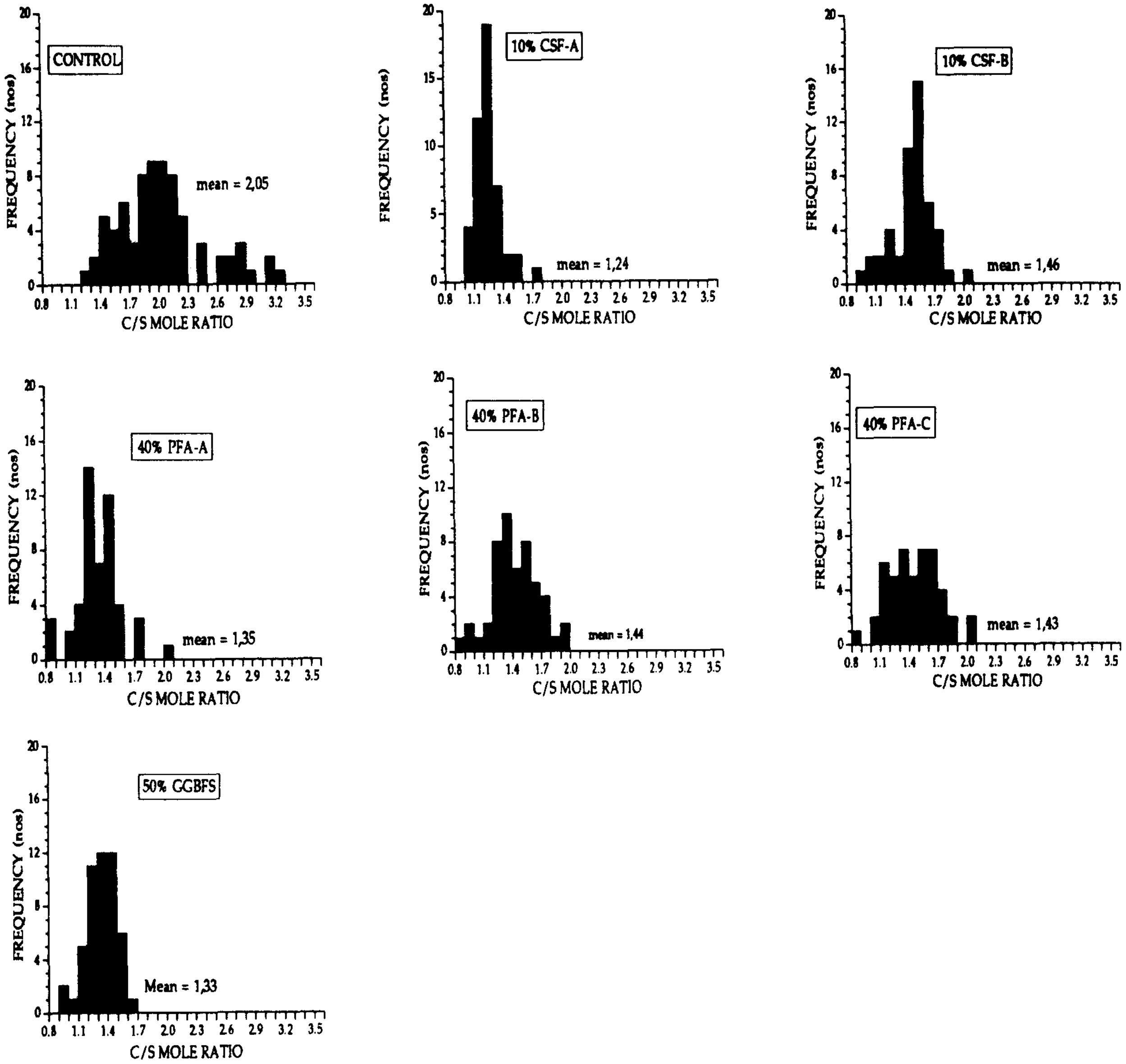

FIGURE 1. Frequency distribution of the C/S mole ratio in cement hydration products as measured in the 3-year old concrete samples using the EPMA.

C/A MOLE RATIO IN CEMENT HYDRATION PRODUCTS. The C/A mole ratio in hydrates also tends to decrease by addition of SCM in concrete (Figure 4B). An example of this behavior is shown in Figure 2. In spite of the scattering between the results, it is clear from this figure that the C/S and C/A mole ratios decrease with the utilization of the PFA-B. As mentioned before, the alumina content in the original OPC + SCM mixture influences the alumina content in corresponding hydrates. Indeed, the lowest C/A values are obtained with the three PFAs, followed by the GGBFS, which contain the highest amounts of alumina.

COMPARISON WITH OTHER RESULTS FROM LITERATURE. A mean C/S mole ratio of 2.05 was obtained in the present study for the OPC concrete, which is close to the highest values found in literature by Uchikawa [2] (2.03) and by Thomas et al. [9] (1.94). On the other hand, the mean C/S values obtained in this study for all blended concretes fall within the variation ranges found in literature (Table 1). From all these results, it is clear that the composition of hydrates may vary in accordance with the type and variety of the SCM tested, as well as with the amount used as cement replacement. However, our results suggest that the variations are more limited than expected from the literature, in particular for PFA. Indeed, the three PFAs tested in this study were covering a wide range of composition, but the resulting hydrates presented quite similar C/S mole ratios (1.35 to 1.44).

ALKALI CONTENT OF CEMENT HYDRATION PRODUCTS. It is usually thought that a low C/S mole ratio hydrate does entrap more alkali than a high C/S mole ratio hydrate

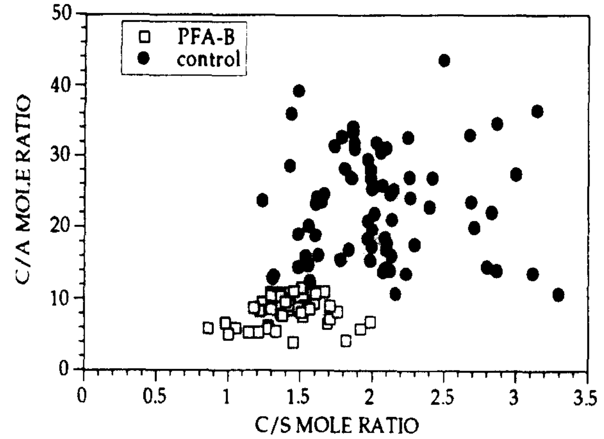

FIGURE 2. C/S mole ratio as a function of the C/A mole ratio in hydrates as measured in the OPC control and PFA-B concretes.

[1]. However, the differences between OPC and blended samples are fairly to very large from one study to another (for instance, from 0.1 to 1.1% K_2O [8], and from 0.58 to 0.76% K_2O [7]). The overall range of alkali contents reported in Table 1 is also quite large, varying from 0.1 up to 1.3% K_2O; for OPC cements only, the K_2O content varies from 0.1 to 0.58%, which corresponds to K_2O/CaO mole ratios from about 0.001 to 0.008. Nevertheless, these results are in good agreement with Taylor [16], who mentions that the K_2O/CaO mole ratio in hydrates from OPC is typically ≈0.01, while it is <0.01 for Na_2O/CaO.

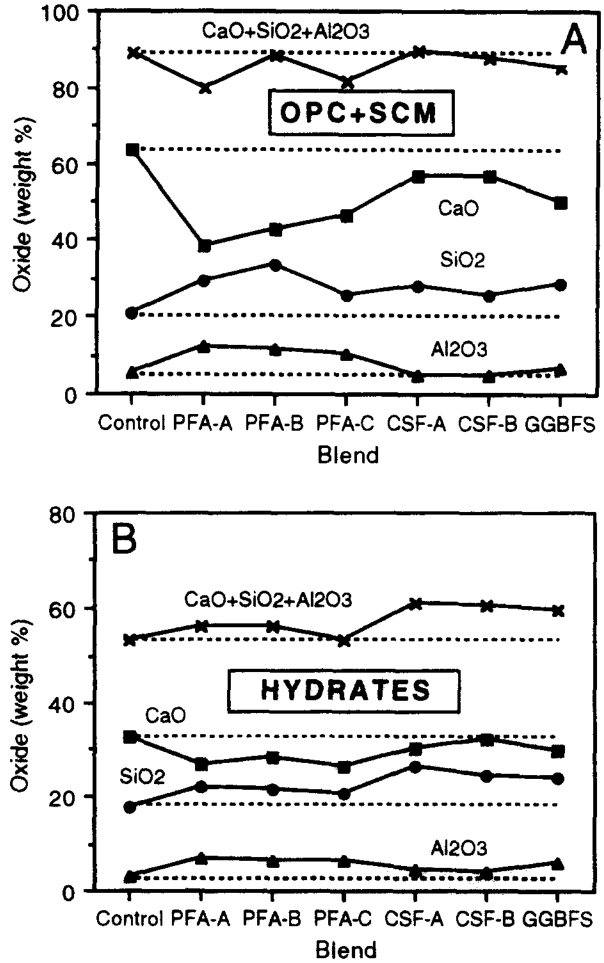

FIGURE 3. Mean contents of major oxides CaO, SiO_2, and Al_2O_3 in: (A) initial anhydrous cementitious mixtures and (B) hydrates of corresponding concretes.

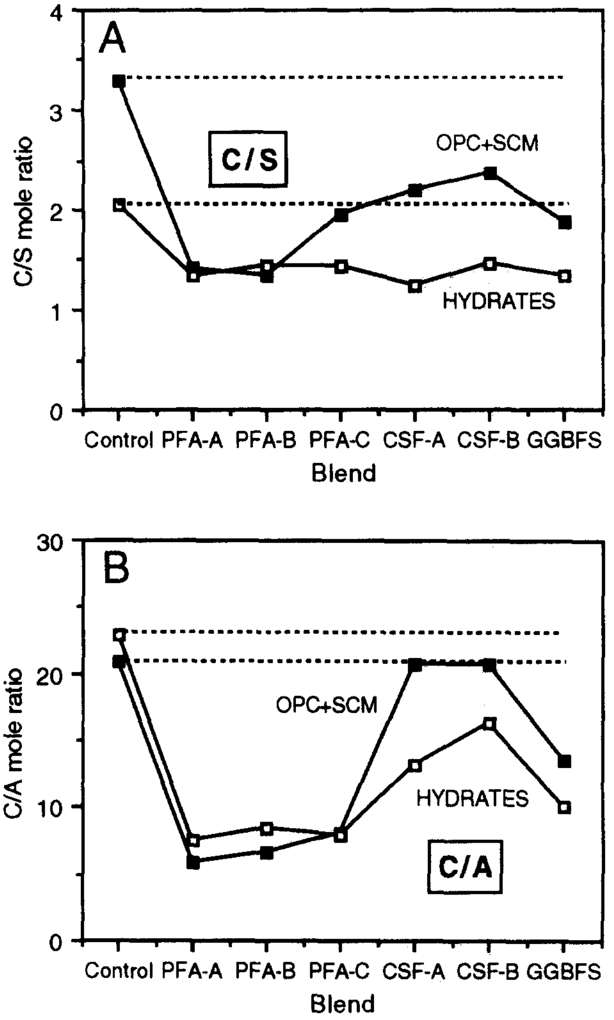

FIGURE 4. Mean C/S (A) and C/A (B) mole ratios in initial anhydrous cementitious mixtures and hydrates of corresponding concretes.

However, the alkali contents of hydrates as measured by EPMA or SEM are considered to be higher than the true values [16,19]. Indeed, significant amounts of alkalies are originally dissolved in the pore solution of concrete or paste specimens; unfortunately, these alkalies are deposited when the pore solution evaporates during specimen preparation or under the high vacuum in the EPMA or SEM, and then are partly adsorbed in hydrates and contribute to give overestimated values. The alternative way used in this study consists in measuring the alkalies in solution using the pore water expression method, and then assuming that alkalies not found in solution are partly bound in hydrates and partly in unreacted particles of the cementitious materials.

Chemistry of Pore Water in Paste Samples

Figure 5A and B shows the alkali concentrations in the pore water of the different paste samples after 1 year of curing. For comparison, the alkali concentrations in the initial mixtures of (OPC + SCM) are presented in Figure 5C with respect to the control (OPC). One can see that the blends with CSF-A and GGBFS are the only ones containing less alkali than the control. As observed in Figure 5 and discussed elsewhere in more detail [20], the alkali concentration in the pore water is greatly influenced by the type and the chemical composition of the SCM used, as well as the SCM:OPC ratio. Moreover, when SCM particles react with the highly basic pore solution, the alkalies that they contain are released, with a fraction remaining in the concrete pore solution and the rest being entrapped in hydrates [21]. A threshold value of 0.6 mol/L of NaOH + KOH was clearly observed at 1 year, under which concrete expansion was always reduced to less than 0.04%, which is the maximum expansion tolerated by the Canadian Standard Association [18]. All cementitious mixtures except with PFA-C and CSF-B show reduction by more than 50% in the alkali concentration compared with the control (Figure 5B), even with SCMs containing much more alkali than the cement (PFA-A, PFA-B): 51, 58, 64, and 58% reduction, with CSF-A, PFA-A, PFA-B, and GGBFS, respectively. These four SCMs proved to be effective in reducing concrete expansion in the presence of highly alkali-silica reactive aggregates [18]. CSF-B also decreases the alkali concentration in the pore solution but to a lesser extent (28%). This silica fume is less effective in reducing concrete expansion as a result of a relatively high alkali content and relatively low silica and alumina contents [18]. On the other hand, PFA-C was totally ineffective in reducing concrete expansion due to alkali-silica reactivity [18]. This fly ash increased the alkali concentration in the pore solution by 74%, but this increase was lower than expected from the initial cementitious mixture for which the alkali content (4.05% Na_2O_{eq}) is almost four times the one of the control (1.05% Na_2O_{eq}). The above results thus indicate that more alkali ions are bound to hydrates from blended cements than from OPC, even with PFA-C.

Estimation of Alkalies in Hydrates, and Alkali Partitioning Between Pore Water and Hydrates

Using the above results, an attempt is made hereafter to estimate, at 1 year, the alkali content and the parti-

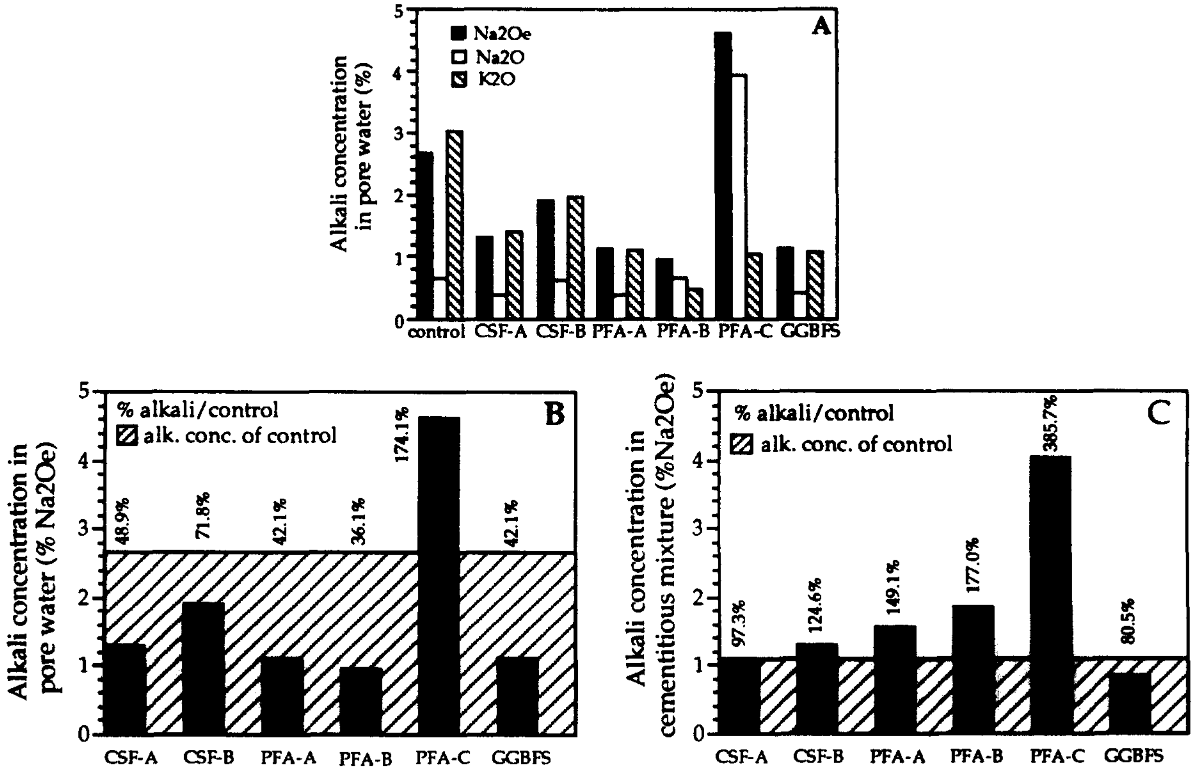

FIGURE 5. Alkali concentration in pore solution expressed from blended paste samples after 1 year of curing at 38°C and 100% RH (A and B) and initial anhydrous cementitious mixtures (C).

tioning between the alkalies in pore water, those bound in hydrates, and those remaining in unreacted cementitious materials. First, the amount of hydrates and pore water must be known. Starting with a 100-g anhydrous mixture of OPC + SCM to which 50 g of water is added, these values can be estimated using eqs 1 and 2, assuming that the paste samples did not gain additional water since they were stored inside capsulated plastic bottles:

$$\text{hydrates (g)} = [\text{OPC (g)} \cdot R_{\text{OPC}} \cdot (1 + BW_{\text{OPC}})] + [\text{SCM (g)} \cdot R_{\text{SCM}} \cdot (1 + BW_{\text{SCM}})] \quad (1)$$

$$\text{pore water (g)} = 50 - [\text{OPC (g)} \cdot R_{\text{OPC}} \cdot BW_{\text{OPC}}] - [\text{SCM (g)} \cdot R_{\text{SCM}} \cdot BW_{\text{SCM}}] \quad (2)$$

where R is the fraction of reacted OPC or SCM after 1 year, relative to anhydrous material, and BW is chemically bound water in OPC or SCM hydrates, relative to anhydrous material. (The chemically bound water includes water present in interlayer spaces, or more firmly bound, but not that present in pores larger than interlayer spaces. The content of chemically bound water is approximately that retained on equilibration at 11% RH of a sample not previously dried below saturation. For fully hydrated pastes of typical cements, it is about 32%, referred on the ignited weight [16]).

The fraction of reacted cement (R) and the percentage of chemically bound water (BW) are unknown and were estimated from measurements reported by Taylor [16]. For a 1-year old OPC paste made with a water: cement (w:c) ratio of 0.5, a value of 95% was considered for R and 32% for BW [16]. The fraction of reacted slag was estimated at 60% (55% at 23°C in ref 16). The values corresponding to PFA are not so easily estimated, since the amount of hydrates formed varies with the amount of reactive phases in the PFA. After 1 year, we use estimates of 25% for the fraction of reacted PFA-A, which contains many of nonreactive phases like quartz, mullite, magnetite, and hematite. Values of 30 and 35% were used for PFA-B and PFA-C, respectively (21% after 3 months in ref 16). These values are based on the portlandite consumption in the cement paste by the corresponding SCM and on their nonreactive mineral content. For CSF, the amount of reacted material was taken as 100% less the loss on ignition (LOI) and the iron content, which gives about 95 and 85% for CSF-A and CSF-B, respectively. The BW in corresponding hydrates was estimated at 23% for CSF, PFA, and GGBFB [16].

For the mass balance of alkalies, we also need an estimate of the amount of alkalies released after 1 year by the cement and by the SCM. Based on a previous study [21], 100% of alkalies from the cement are expected to have been released. Estimates of 85, 100, and 85% are used for PFA, CSF, and GGBFS, respectively. These percentages are naturally higher than the corresponding percentage of reacted materials since the alkalies tend to be incorporated in the most soluble (sulfates, carbonates) or reactive (glass) phases of cements and supplementary cementing materials.

Using the above estimated values given in the Appendix, one can now calculate the alkali content in hydrates and the partitioning of the alkalies released by the cementitious materials in hydrates and pore water. For comparison, the calculations have also been made by modifying the above estimates within reasonable limits. The alkali contents of hydrates then obtained are not significantly different than those given in the Appendix, which indicate the following:

- The alkali content of OPC hydrates is estimated to be about 0.43% Na_2O_{eq}, and the proportion of alkalies released by the cement and entrapped in hydrates is about 51%. The latter proportion is in quite good agreement with Taylor [16], who indicated 59% for Na ions and 48% for the much more aboundant K ions, for a 1-year old OPC paste made with a w:c ratio of 0.5.
- The addition of PFA resulted in hydrates (1.25 to 2.41% Na_2O_{eq}) that contain effectively much more alkali than OPC hydrates. As a result, a higher proportion (63 to 84%) of the total amount of alkalies released by the cementitious materials are entrapped in hydrates.
- The addition of CSF also increased significantly the alkali content of hydrates (0.61 and 0.74% Na_2O_{eq}) and the amount of released alkalies entrapped in these (70 to 74%), despite the relatively low 10% cement replacement used.
- However, the hydrates formed in the presence of 50% GGBFS do not contain significantly more alkalies (0.49% Na_2O_{eq}) than OPC hydrates, nor do they entrap a much higher proportion of the alkali released by the cementitious materials (61%). This suggests that the effectiveness of the GGBFS tested in suppressing alkali-aggregate reaction (AAR) expansion is mostly due to alkali dilution.

For all specimens tested, the calculated alkali content in the hydrates does not correlate with either the C/S mole ratio in these hydrates or the alkali concentration of the pore water. However, the correlation is good between the alkali content of hydrates and the alkali content of the initial cementitious mixture as presented in Figure 6. The alkali content of the initial mixture in turn does not correlate with the alkali content of the pore water. In other words, the low C/S hydrates formed in the presence of all SCM types have the possibility to include more alkalies, but their alkali content will remain low in the presence of low alkali cementitious mixtures (for instance, with the GGBFS tested). It is likely that the hydrates formed in the presence of a more alkaline GGBFS would also contain more alkali than OPC hydrates. In this case, the effectiveness of the SCM against AAR would not be related only to alkali dilution.

Conclusion

Expression of pore water from hardened cement pastes and measurements of hydrates in blended concrete using the EPMA show the following:

- The C/S mole ratio in hydrates varies irregularly from point to point but is statistically normally distributed at the level of volume sampling (μm^3), even in the presence of two cementitious materials of very different composition (OPC and SCM).
- The composition of cement hydration products is modified when SCM is added to the cement. The C/S and C/A mole ratios are significantly lowered.
- However, the C/S ratio in hydrates is not significantly different from one type of SCM to another.
- All blended pastes except the one with the very alkali-rich PFA showed a drop in the alkali concentration of the pore water compared with the control, even with SCMs containing much more alkali than the cement. At first, this suggests that higher amounts of alkali ions are incorporated in hydrates from blended mixtures compared with OPC hydrates.

Some calculations based on the above results and a number of realistic approximations indicated the following:

- The low C/S hydrates produced in the presence of SCM can contain much more alkali than hydrates from OPC, and therefore may decrease the alkalinity and the pH of the pore water and reduce expansion due to alkali silica reactivity, provided the SCM alkali content is not too high and the amount used as cement replacement is high enough. SCMs with excessive alkali contents, like the very high alkali PFA tested, rather increase the alkali concentration in the pore water and are totally ineffective in controlling expansion due to alkali-silica reactivity, in spite of largely decreasing the C/S mole ratio and increasing the alkali content of hydrates.
- The effectiveness of the GGBFS tested in this study with respect to alkali-silica reaction (ASR) seems mostly related to an alkali dilution effect. Indeed, the alkali content in hydrates from the GGBFS mixture and the proportion of alkali released in pore water by the cementitious materials are not significantly higher than with OPC only. However, this behavior is attributed to the low alkali content of the initial mixture and should not apply to any blended cements containing GGBFS.
- Indeed, for all specimens tested, the calculated alkali content in the hydrates does not correlate either with the C/S mole ratio in these hydrates or with the alkali concentration in the pore water; however, the correlation is good with the total alkali content of the initial mixtures of cementitious materials (OPC or OPC + SCM). In other words, the low C/S hydrates from blended cements will contain more alkali provided the initial mixture has a relatively high alkali content; this was not the case in the presence of the low alkali GGBFS tested.

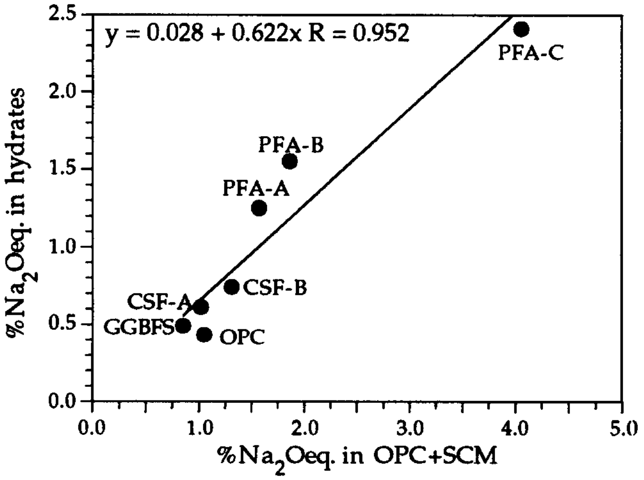

FIGURE 6. Calculated alkali content in hydrates of 1-year old blended paste samples as a function of the alkali content of initial anhydrous cementitious mixtures.

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Appendix: Calculation of the Alkali Contents of Hydrates and of the Partitioning of the Released Alkalies from the Cementitious Materials Between Hydrates and Pore Water

Paste Sample	OPC g [a]	OPC $\%Na_2O_{eq}$ [b]	SCM g [c]	SCM $\%Na_2O_{eq}$ [d]	OPC + SCM g Na_2O_{eq} [e]^A	Mix Water g [f]	Pore Water $\%Na_2O_{eq}$^{B} [g]
OPC	100.00	1.05%	0.00	1.05%	1.05	50.00	2.63%
PFA-A	60.00	1.05%	40.00	2.34%	1.57	50.00	1.11%
PFA-B	60.00	1.05%	40.00	3.07%	1.86	50.00	0.95%
PFA-C	60.00	1.05%	40.00	8.55%	4.05	50.00	4.58%
CSF-A	90.00	1.05%	10.00	0.77%	1.02	50.00	1.29%
CSF-B	90.00	1.05%	10.00	3.63%	1.31	50.00	1.89%
GGBFS	50.00	1.05%	50.00	0.64%	0.85	50.00	1.11%

^{A}[e] = ([a][b]) + ([c][d]). ^{B}Measurement of pore solution expressed under high pressure (560 MPa).

Paste Sample	% Hydrated OPC [h]^A	% Hydrated SCM [i]^A	% Alkali Released from SCM [j]^A	$\%H_2O$ in OPC Hydrates [k]^B	$\%H_2O$ in SCM Hydrates [l]^B	Total Hydrates (g) [m]^C	Chemically Bound Water (g) [n]^D
OPC	95%			32%		125.40	30.40
PFA-A	95%	25%	85%	32%	23%	87.54	20.54
PFA-B	95%	30%	85%	32%	23%	90.00	21.00
PFA-C	95%	35%	85%	32%	23%	92.46	21.46
CSF-A	95%	95%	100%	32%	23%	124.55	29.55
CSF-B	95%	85%	100%	32%	23%	123.32	29.32
GGBFS	95%	60%	85%	32%	23%	99.60	22.10

^{A}Estimated value. ^{B}Chemically bound water, relative to anhydrous OPC or SCM; estimated value.
^{C}[m] = ([a][h][1 + k]) + ([c][i][1 + l]). ^{D}[n] = ([a][h][k]) + ([c][i][l]).

Paste Sample	Residual Pore Water (g) [o] = [f] − [n]	g Na_2O_{eq} in Pore Water [p] = [o][g]	g Na_2O_{eq} in Hydrates [q]^A	$\%Na_2O_{eq}$ in Hydrates [r] = [q]/[m]	% of Alkali Released in Pore Water [s] = [p]/ [p] + [q]	% of Alkali Released in Hydrates [t] = [q]/ [p] + [q]	Hydrates Alkali Ratio^B [u] = [r]/ 0,43
OPC	19.60	0.52	0.53	0.43%	49.1%	50.9%	1
PFA-A	29.46	0.33	1.10	1.25%	22.9%	77.1%	2.94
PFA-B	29.00	0.28	1.40	1.55%	16.5%	83.5%	3.64
PFA-C	28.54	1.31	2.23	2.41%	37.0%	63.0%	5.66
CSF-A	20.46	0.26	0.76	0.61%	25.8%	74.2%	1.43
CSF-B	20.69	0.39	0.92	0.74%	29.9%	70.1%	1.74
GGBFS	27.90	0.31	0.49	0.49%	38.9%	61.1%	1.15

^{A}[q] = ([a][b]) + ([j][c][d]) − [p]. ^{B}Relative to the alkali content of hydrates in the control.