RELATIONSHIPS BETWEEN PORTLANDITE DEPLETION, AVAILABLE ALKALIES AND EXPANSION OF CONCRETE MADE WITH MINERAL ADMIXTURES

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The portlandite content (TGA), pore solution composition (high pressure extraction method) and available alkali content (ASTM C311) of cement pastes made with various mineral admixtures were measured after 7, 28, 84 and 364 days of curing. Results were compared to expansions obtained with two reactive aggregates in the CAN/CSA A23.2-14A Concrete Prism Method. The best correlation was obtained between the alkali drop in pore solution and the expansion reduction while portlandite depletion is just an artefact. Also, the total alkali content instead of the available alkali content should be used as a conservative measurement of the mineral admixture active alkali content.

INTRODUCTION

The utilization of mineral admixtures is one of the most popular ways to minimize the deleterious expansion due to alkali silica reaction. However, the behavior of mineral admixtures is not completely understood. Some authors such as Chatterji & Taulow (1) and Chatterji (2) considered that the depletion of $Ca(OH)_2$ has a major role in controlling expansion while others such as Hobbs (3) and Nixon & Page (4) indicated that admixtures reduce the alkalinity in the pore solution.

The objective of this study was to understand the behavior of various types of mineral admixtures in relation to the amount of portlandite and the content of available alkalies in the blended cements. These results were compared to expansions obtained with two very reactive aggregates in the CAN/CSA-A23.2-14A Concrete Prism Method.

MATERIALS AND METHODS

The effectiveness of one ground granulated blast furnace slag, two condensed silica fumes (high silica/low alkali, low silica/high alkali), and three fly ashes (low alkali/low calcium, low alkali/moderate calcium, high alkali/high calcium) was tested in the presence of two alkali-reactive aggregates from Canada, one siliceous limestone (Spratt Quarry) and one rhyolitic tuff (Beauceville Quarry). The chemical compositions of cements and mineral admixtures are given in Table 1.

The CAN/CSA-A23.2-14A Concrete Prism Method was used as a reference test with the two aggregates, cement B, and various mineral admixture contents (0, 5, 10% silica fume; 0, 20, 40% fly ash and 0, 35, 50% slag). The samples were tested with the alkali content increased to 1.25% (Na_2O equiv.) of the mass of cement, by adding NaOH to the mix water, a cement + admixture content of 350 kg/m^3 and a water/cement of 0.5. Cement B was used for all concrete samples.

TABLE 1 -- Chemical composition of mineral admixtures and cements

	PFA			CSF		GBFS	CEMENT	
	A	B	C	A	B	A	A	B
Oxide (%)								
SiO2	42.20	53.90	32.59	94.17	74.60	36.60	20.47	20.66
Al2O3	21.60	20.90	17.93	0.21	0.59	8.00	5.51	4.62
Fe2O3	27.60	3.52	5.94	0.32	6.54	0.67	2.45	3.11
TiO2	-	-	1.17	0.00	0.00	-	0.24	0.28
MnO	-	-	0.03	0.07	0.38	-	0.05	0.05
MgO	0.92	1.11	4.12	0.47	1.56	13.70	2.82	2.31
CaO	1.87	12.00	20.70	0.50	0.40	37.20	63.12	61.76
Na2O	0.66	2.74	8.08	0.00	1.68	0.44	0.29	0.20
K2O	2.55	0.50	0.72	1.17	2.97	0.31	1.16	0.82
P2O5	-	-	0.59	0.04	0.00	-	0.13	0.26
Cr2O3	-	-	0.01	0.00	0.03	-	0.00	0.01
SO3	1.10	0.09	1.48	0.12	0.81	3.97	2.60	2.98
LOI	1.85	0.57	0.96	2.77	7.34		0.81	2.82
Total	100.35	95.33	94.32	99.84	96.90	100.89	99.65	99.88
Alk.(eq.Na2O)	2.34	3.07	8.55	0.77	3.63	0.64	1.05	0.74

A certain amount of alkalies can be released from the mineral admixtures and carried into the pore solution. These alkalies become available for potential alkali silica reaction. To measure this alkali content, two methods were used: [1], ASTM C311 standard method and the modified version proposed by Barlow & Jackson (5) and Chau Lee (6), and [2], high-pressure pore solution extraction method .

[1] The ASTM C311 method was used to determine the amount of alkalies available from mineral admixtures. The test consists of mixing 5g of mineral admixture, 2g of calcium hydroxide and 10 ml of water for 28 days at 38°C. After the curing time, the available alkalies were extracted with water and analysed by flame photometry. According to some authors (5,6), this test tends to underestimate the ultimate active alkali content and alkalies continue to be released after 28 days. This is the reason why the same procedure was also used to determine the available alkalies from cement A and cement A+admixture combinations, without calcium hydroxide. Moreover, measurements were done at 7 days, 1, 3 and 12 months.

[2] Cement-admixture paste samples were made with the same mineral admixture contents and the same water/cement ratio (0.5) as for the concrete prism samples. After curing periods of 7 days, 1, 3 and 12 months at 38°C, pore solutions were extracted by a high-pressure method first described by Longuet (7). The solutions were analysed by flame photometry for sodium and potassium. The alkalinity was also measured by acid titration using methyl orange as indicator (end point at pH ~3.8).

Duplicates of cement-admixture pastes were also made to measure the portlandite content by thermogravimetry (SETERAM TG-DTA 92) after the same curing times. The portlandite decomposed between ~435 to 550°C and a correction was made for carbonatation.

RESULTS AND DISCUSSION

ASTM C311 standard and modified procedures

Figure 1 presents the available alkalies as a function of time in presence of $Ca(OH)_2$, in equiv. Na_2O (Figure 1A) and percent of the total alkali content (Figure 1B). They increased with time except with the silica fumes A and B. Table 2 presents the available alkalies for each mixture in percent of the total alkali content and of the total alkali in admixtures, taking into account that the cement liberated 92.8, 97.5, 99.1 and 92.0% of its alkalies after 7, 28, 84 and 364 days of curing respectively. Figure 2 shows an example of active alkalies (% of total Na_2O eq.) for the cement, the fly ash A and cement + PFA-A mixtures as a function of time (Figure 2A) and mineral admixture content (Figure 2B). The proportion of available alkalies released by admixtures in presence of cement is generally greater than in the standard ASTM C311. In presence of $Ca(OH)_2$, the initial pH was ~ 12.5. This value is low compared to more aggressive concrete pore solution which can reach an hydroxide ion concentration around 0.7N (pH>13.5) with a high alkali cement. At the beginning, the admixture had not enough time to react, therefore, did not liberate much alkali and produced dilution. In the long term the total available alkalies are greater than with cement only. The dilution effect no longer takes place. In addition, the admixture content influenced the percentage of available alkali from admixtures when cement-admixture combinations were tested (Figure 2B), which decreased when increasing the admixture content. This was also observed by Barlow & Jackson (5). With a greater amount of admixture, there is a lower amount of portlandite in the paste, therefore, the pozzolanic CSH may present a lower Ca/Si and can trap more alkalies which are not released in the ASTM C311 modified test (Bhatty & Greening (8) and Glasser & Marr (9)).

TABLE 2 -- Available alkalies from different mineral admixtures

	% of available alkalis in the total alkali content of each mixture				% of alkalis liberated by the admixtures (excluding those available from the cement)			
MIX	7d	28d	84d	364d	7d	28d	84d	364d
0% (cement A)	92.8	97.5	99.1	92.0				
CSF-A 5%	89.6	99.3	98.3	96.3	100.0	100.0	100.0	100.0
10%	86.3	96.6	95.9	98.3	55.2	100.0	100.0	100.0
100%(standard)	100.0	100.0	100.0	89.9				
CSF-B 5%	84.6	80.2	75.4	83.7	65.8	12.7	-	45.5
10%	74.8	84.6	67.7	75.6	40.2	63.8	-	37.2
100% (standard)	63.4	60.6	42.7	51.7				
PFA-A 20%	65.8	78.9	84.7	92.0	25.6	54.3	67.3	91.8
40%	44.1	63.7	69.4	70.1	14.3	44.2	52.6	55.6
100%(standard)	12.8	42.8	55.2	55.8				
PFA-B 20%	61.3	81.4	88.5	87.4	24.5	66.0	80.4	82.6
40%	44.1	-	64.6	72.1	21.5	-	49.3	62.8
100%(standard)	14.6	42.8	51.8	49.7				
PFA-C 20%	79.4	-	94.2	93.4	75.1	-	94.1	94.5
40%	62.1	77.8	87.7	86.6	57.3	75.1	86.5	85.8
100% (standard)	53.1	74.8	87.1	91.0				
35%	80.9	100.0	89.2	90.5	59.7	100.0	74.5	89.7
GBFS-A 50%	73.6	91.2	89.2	85.3	50.3	89.5	81.3	76.7
100%(standard)	34.7	49.7	50.5	69.8				

These results demonstrate that the standard C311 tends to underestimate the percent of alkali available from PFA's and GBFS's because:

1) after 28 days of curing these admixtures continue to release significant amounts of alkalies (Figure 1A);
2) the initial pH is low compared to the average concrete pore solution;
3) this method does not take account for alkalies bound in pozzolanic CSH.

To measure the total available alkali released by admixtures, the method used must prevent the formation of pozzolanic CSH. No calcium must be available to react with the mineral admixture, so no cement should be used. This is for pozzolanic admixtures; for hydraulic ones the problem persists. So, the testing method should specify

1) a curing time long enough to approch the maximum;
2) pH equal to that found in concrete pore solution;
3) no possibility for the admixture to produce pozzolanic CSH.

Note that even though the method tends to under-estimate the total available alkalies, the values obtained often approched 100% in the long term (CSF-A 100%, CSF-B 65.8%, PFA-A 91.8%, PFA-B 82.6%, PFA-C 94.5% and GBFS-A 100%). These results suggest that the total alkali content, instead of the available alkali content should be used as a conservative measure of the alkali content.

High pressure pore solution extraction method.

Figure 3 and Table 3 show the alkalies in pore solution (% equiv. Na_2O) as a function of time. The samples CSF-B 5% (at 84 days), PFA-C 20% and 40% (at any time) present higher concentrations in pore solution than the high alkali control. In the presence of silica fume, the alkali content tends to increase with time. For the other admixtures (except PFA-C) there is a diminution of the alkali with time. The pulverised fly ash rich in alkali (PFA-C, 8.55% Na_2O equiv.) contains thenardite (Na_2SO_4) identified by XRD. This mineral is easily soluble then rapidly available.

When the pH is high, [Na] + [K] ~ [OH] because other species are insignifiant compared with alkali ions. The relation between the alkalinity measured and the summation $Na^+ + K^+$ is a straight line for this pH range (Figure 4). The hydroxide ion concentration given in Table 3 are very high (0.857M for the control at 1 year compared to 0.689, 0.669 and 0.646 M at 7, 28 and 84 days). By that time, with a larger proportion of the cement hydrated, less pore solution must have remained, which may explain the increase in alkali concentration. After 149 days of curing, Diamond (10) obtained 0.83N (Na + K) with an high alkali cement (0.91% Na_2O equiv.).

Figure 5 shows that all admixtures (except PFA-C) reduced at 1 year the alkali (and hydroxide) ion in the pore solution compared to the control, even for admixtures containing much more alkali than the control (SF-B, PFA-A, PFA-B), while the ASTM C311 tests yielded available alkali contents usually greater than for the control. This suggest that significant amounts of alkalies are trapped in pozzolanic CSH, while being released in solution in the ASTM C311 test. Moreover, results on Figure 5 shows that, the higher the admixture content, the lower are the alkalies in the pore solution, the more abundant are the pozzolanic CSH, and the lower is the expansion of the corresponding concrete (Figure 9).

TABLE 3 -- Hydroxide ion concentration and alkali depletion in pore solution

		$Na^+ + K^+$ (M)				alkali depletion (%) compared to the control			
	time	7d	28d	84d	364d	7d	28d	84d	364d
T (control)		0.689	0.669	0.646	0.857	0.0	0.0	0.0	0.0
CSF-A	5%	0.475	0.493	0.534	0.681	31.3	26.2	17.5	20.7
	10%	0.261	0.305	0.307	0.420	62.1	54.4	52.5	51.1
CSF-B	5%	0.389	0.426	0.705	0.895	43.5	36.4	(9.5)	(4.1)
	10%	0.252	0.214	0.377	0.617	63.6	67.9	41.5	28.2
PFA-A	20%	0.549	0.459	0.406	0.510	20.6	31.3	37.0	40.6
	40%	0.394	0.290	0.268	0.361	43.0	56.7	58.5	57.9
PFA-B	20%	0.486	0.435	0.377	0.492	29.9	35.0	41.5	42.9
	40%	0.385	0.294	0.238	0.310	44.4	56.0	63.0	63.9
PFA-C	20%	1.399	1.498	1.201	1.636	(102.8)	(79.7)	(79.5)	(90.6)
	40%	1.718	1.525	1.499	1.493	(148.6)	(124.2)	(137.0)	(74.1)
GBFS-A	35%	0.446	0.411	0.399	0.493	35.5	38.6	38.0	42.5
	50%	0.348	0.289	0.268	0.362	49.5	56.8	58.5	57.9

Portlandite content in cement-admixture pastes

Figure 6 presents the percent of portlandite in pastes as a function of time. All mineral admixtures consumed portlandite but some was still remaining after 1 year of curing. The lowest content (4.58%) was obtained with 40% PFA-C. Figure 7 shows the portlandite consumption with time normalized with respect to the cement content. For example, the mix composed of 20% PFA-A contains 13.90% $Ca(OH)_2$ at 28 days. At the same time, the control contains 20.44% $Ca(OH)_2$. If the admixture was inert, the paste should present 80% x 20.44% = 16.35% $Ca(OH)_2$. The admixture then consumed 2.45% which corresponds to 2.45/16.35=15.00% consumption. Increasing the mineral admixture content increased also the portlandite depletion because there is more pozzolanic reaction. The ground granulated blast furnace slag depleted just a little portlandite. This admixture behaves hydraulically. It does not require portlandite to produce CSH. Also, Figure 7 shows that PFA-C reacted very rapidly. At 7 days, this fly ash depleted 24.6 and 48.3% of the portlandite in paste when using 20% and 40%, respectively. The silica fumes exhibited the same behavior. During the first seven days, they showed the highest portlandite depletion rate. After 84 days, these mixtures no larger consumed any portlandite.

Relationships between previous results and expansion measured in the CAN/CSA A23.2-14A Concrete Prism Method.

The expansion values of all admixture combinations with the two reactive aggregates are listed in Table 4. This table also presents the percent expansion of concrete prisms after 6, 12 and 18 months of curing at 38°C. Figure 8 presents the portlandite depletion in pastes as a function of concrete expansion. There is no relation between these values. The paste (PFA-C) with the lowest portlandite content corresponds to a very expansive concrete. Moreover, 5% silica fumes led to significant portlandite decrease but the corresponding concretes expanded more than the control. However, for the same admixture, increasing the content reduced both portlandite and expansion.

Figure 9 shows a good correlation between the drop of alkali ions in pore solution and expansion reduction in concrete, for all samples tested. All mixes capable of reducing the alkali content to under 30% of the control were nonreactive in concrete. The mix with 10% CSF-B is just at the limit. This sample presented an expansion of 0.048% in presence of the rhyolitic tuff and 0.019% with the Spratt limestone after one year of curing. However, at 18 months, the expansions were 0.097% and 0.055% respectively, which are significantly high. The different behavior of the two aggregates can be explained by the possibility that the tuff aggregate liberate alkalies in pore solution. Increasing the admixture content increased the drop of alkalies in pore solution and reduced the expansion. Figure 10 shows the drop of alkalies in pore solution as a function of portlandite depletion. Again no relation connects connects these values. The mixes with PFA-C consumed more portlandite (67%) but increased greatly the alkali concentration in pore solution (+90%). Another sample (PFA-B) consumed 54% of portlandite and depleted a large amount of alkalies (-51%) in pore solution.

TABLE 4 -- Expansion values after 6, 12 and 18 months of curing

		RHYOLITIC TUFF			SPRATT LIMESTONE		
METHOD		CAN/CSA A23.2-14A			CAN/CSA A23.2-14A		
MIX		Percent expansion at different ages			Percent expansion at different ages		
		6m	12m	18m	6m	12m	18m
0% control		.152	.243	.250	.161	.276	.301
CSF-A	5%	.015	.322	.368	.010	.183	.232
	10%	-.009	.006	.015	.000	.007	.013
CSF-B	5%	.096	.333	.368	.036	.221	.257
	10%	-.005	.048	.097	.000	.019	.055
PFA-A	20%	-.011	.009	.023	.003	.011	.027
	40%	-.010	-.013	-.011	-.025	-.029	-.034
PFA-B	20%	-.011	.004	.013	-.013	-.006	-.002
	40%	-.011	-.014	-.004	-.014	-.016	-.016
PFA-C	20%	.166	.237	.261	.076	.134	.149
	40%	.063	.121	.142	.034	.081	.095
GBFS-A	35%	-.004	.035	.043	.002	.007	.016
	50%	.004	.007	.006	.000	-.002	-.003

The best correlation was obtained between the drop of alkalies in the pore solution and the reduction of expansion (Fig. 9). A threshold in alkali concentration (or hydroxide ion) was observed around 0.55M (Figure 11) below which there is no expansion. This value is high compared to values proposed by some authors, for instance 0.25M suggested by Diamond (10) for alkali-silica reactivity, and 0.3M proposed by Kolleck et al. (11) for fly ash.

Subsequently, concrete tests were made with those mixtures which showed the best expansion reduction (PFA-A 40%, PFA-B 40%, CSF-A 10% and GBFS-A 50%) but with the alkali content increased to 3.0% (eq. Na_2O) of the mass of cement by adding more NaOH to the mix water (Fig. 13). These samples were made to determine the influence of the alkali content on expansion. Figure 12 shows that increasing this content produced deleterious expansion even if great amounts of good admixture were used.

CONCLUSION

The results suggest that mineral admixtures liberate nearly all their total alkali content. The high pressure pore solution extraction method was used to determine the hydroxide ion concentration of pastes made with different mineral admixtures. Some mixes had more alkali in pore solution than the control, others much lower amounts. There is no relation between the portlandite depletion with the expansion values. The best correlation was obtained between the alkali drop in pore solution and the reduction of expansion. A threshold in alkali concentration was observed around 0.55M. Below this, no significant expansion occured in corresponding concretes made with two very reactive aggregates. These results confirmed that mineral admixtures incorporate alkalies into hydrates. This is in agreement with a number of workers (8) who said that the composition of calcium silicate hydrates was modified when admixture was added to cement, resulting in a decreased Ca/Si which causes more alkali ions to be entrapped into the hydrates, thereby depleting the alkalinity of the pore solution and reducing expansion due to ASR.

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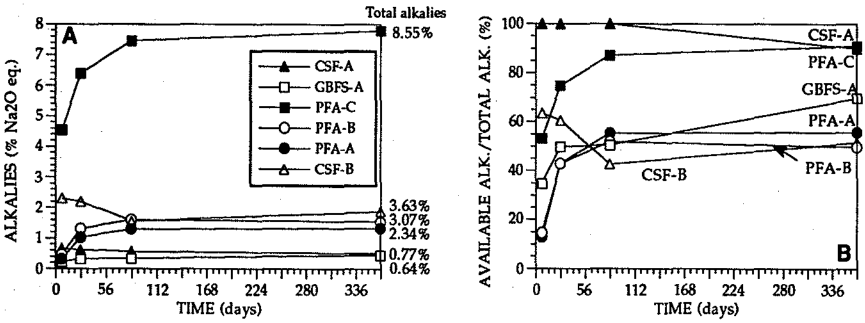


FIGURE 1 -- Available alkalies measured by the ASTM C311 standard as a function of time
a) Na_2O equivalent b) Percent of total alkali content

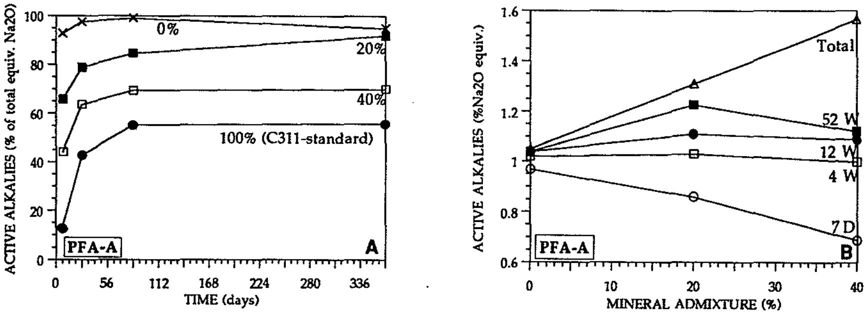


FIGURE 2 -- Active alkalies (ASTM C311 modified for cement-admixture combinations)
as a function of (a) time and (b) fly ash A content

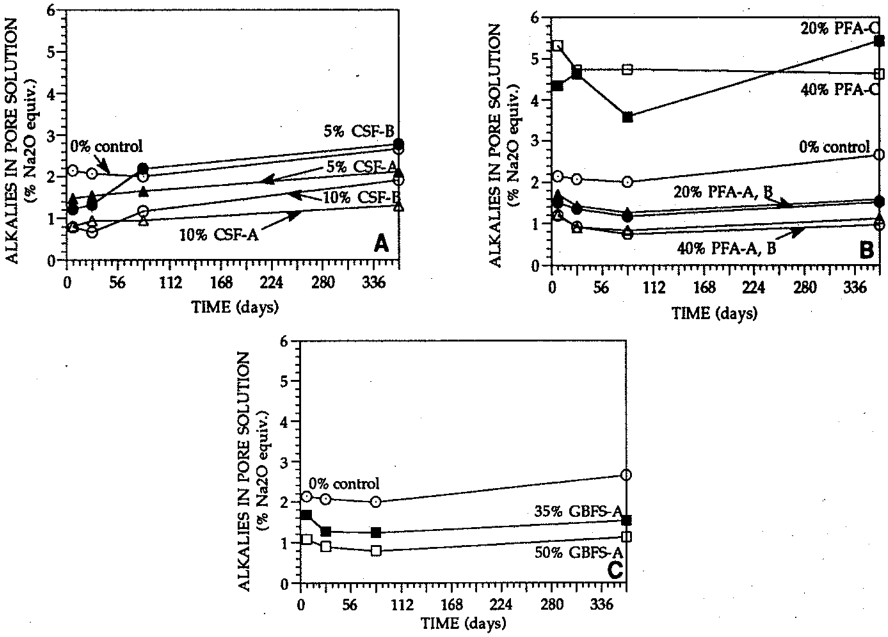
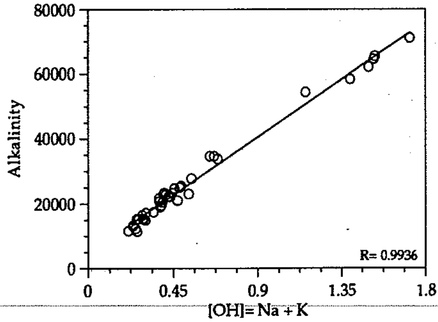


FIGURE 3 -- Alkalies in pore solution as a function of time
a) silica fumes b) fly ashes c) granulated slag



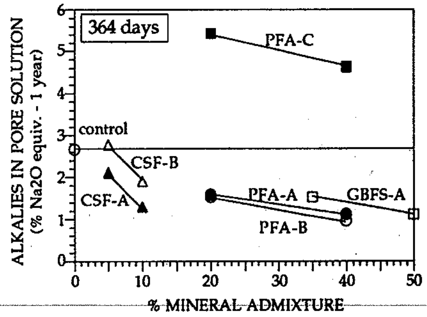


FIGURE 4 --

Alkalinity measured by titration as a function of Na + K content

FIGURE 5 --

Alkalies in pore solution as a function of mineral admixture content

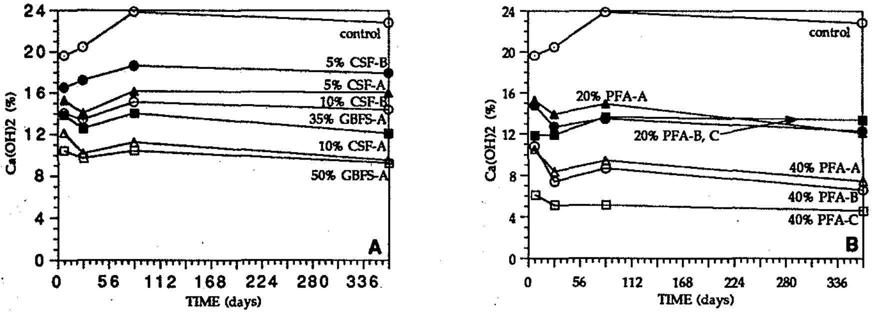


FIGURE 6 -- Portlandite percent in paste as a function of time a) CSF, GBFS b) PFA

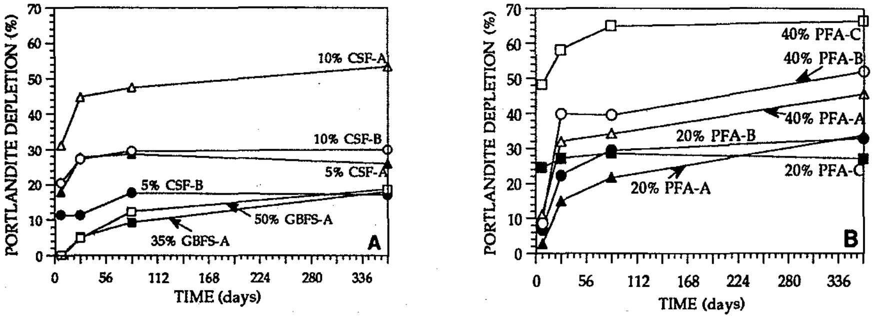


FIGURE 7 -- Portlandite depletion as a function of time a) CSF, GBFS b) PFA

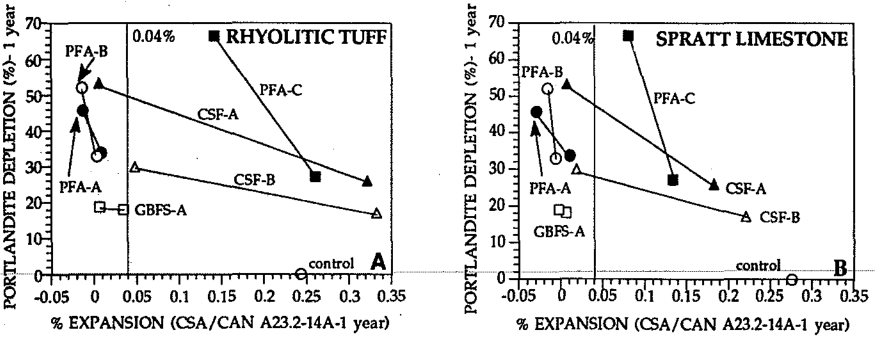


FIGURE 8 -- Portlandite depletion in pastes as a function of concrete expansion
a) rhyolitic tuff b) Spratt limestone

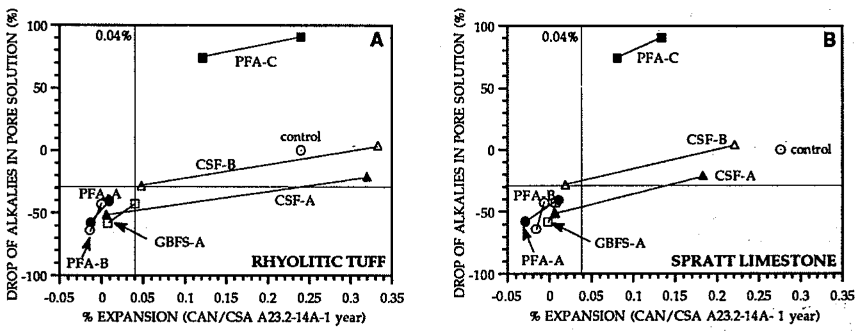


FIGURE 9 -- Relationships between alkali drop in pore solution and concrete expansion
a) rhyolitic tuff b) Spratt limestone

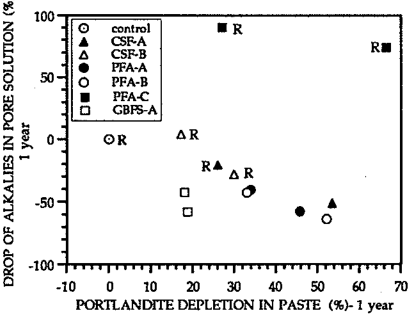


FIGURE 10 --

Alkali reduction in pore solution as a function of portlandite depletion
(R = reactive mixtures in concrete prisms)

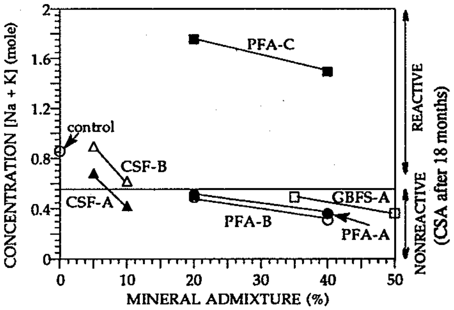


FIGURE 11 --

Hydroxide concentration in pore solution as a function of mineral admixture content
(Threshold around 0.55M)

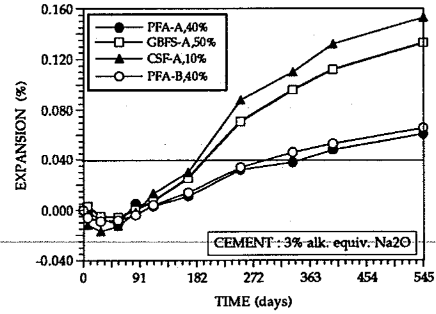


FIGURE 12 -- Concrete expansion as a function of time