Some Long Time Studies of Blended Cements with Emphasis on Alkali-Aggregate Reaction

Muhammad S.Y. Bhatty
Portland Cement Association
Skokie, IL, USA

Nathan R. Greening
Ideal Basic Industries, Cement Division
Laporte, CO, USA

ABSTRACT

Portland cement pastes and blended cement pastes containing opal, calcined shale and Class F fly ash blended at various addition levels were hydrated up to 14 years at 73°F and 100% relative humidity. Pastes cured for 14 years were analyzed for alkalies. It was found that a considerable amount of alkali did not leach out of blended cement pastes compared to portland cement pastes. The amount of alkali retained (not leached) depends on the nature and the amount of pozzolan used. A plot of calcium hydroxide produced as a function of curing time and pozzolanic addition levels up to 14 years showed a maximum which was quite pronounced in some cases. The relationship between C/S mole ratio of blended cements and alkali-aggregate expansion is discussed.

INTRODUCTION

Considerable work has been done over the years on blended cements. In spite of so much interest in the subject, few studies are available which have addressed the long term reactions of such combinations. This paper presents results of long term tests of such combinations with special emphasis on the contribution of pozzolans in controlling the alkali-aggregate reaction. The results of this investigation should help in understanding the role of different pozzolans, and since pozzolans such as fly ash are now being widely used in most parts of the world, a better understanding of the cement-pozzolan system should lead to the use of pozzolans with greater confidence.

EXPERIMENTAL

The materials used in this study consisted of a high alkali Type I portland cement (LTS #14), a low alkali Type I portland cement (LTS #18) and three pozzolans: Nevada opal, calcined Monterey shale, and a Class F Chicago fly ash. Table 1 shows the chemical composition of these materials along with calculated compound composition of the two cements.

Table 1. Chemical Analysis of Cements and Pozzolans (wt%)

	Cements		Pozzolans		
	LTS #14	LTS #18	Opal	Shale	Fly Ash
SiO_2	22.4	21.5	85.2	61.0	47.0
Al_2O_3	4.8	6.1	0.4	10.3	17.3
Fe_2O_3	3.0	2.3	8.4	4.74	18.5
CaO	63.1	64.0	0.4	10.4	7.3
MgO	2.5	2.6	0.1	2.7	0.9
SO_3	1.7	1.8	0.51	0.49	1.86
Na_2O	0.06	0.12	0.08	1.0	1.52
K_2O	1.3	0.13	0.1	1.39	1.96
Total Alkali[a]	0.92	0.21	0.15	1.91	2.81
TiO_2	0.21	0.24	b	0.63	0.76
L.O.I	0.9	1.0	5.1	6.75	2.73
Blaine, m^2/kg	342	327	1000	b	b

Calculated Compound Composition

	LTS #14	LTS #18
C_3S	42.5	44.5
C_2S	32.0	28.0
C_3A	8.2	13.2
C_4AF	9.2	6.8

[a] as equivalent Na_2O
b not determined

Cement and pozzolan blends were prepared by replacing a portion of each cement with three pozzolans at three replacement levels (Table 2) to obtain calcium oxide to silica (C/S) mole ratios of approximately 2.15 ± 0.15, 1.70 ± 0.10 and 1.40 ± 0.10.

Table 2. Amount of Alkali in Original and 14 Years Cured Pastes and Alkali/SiO_2 Mole Ratio in 14 Years Cured Pastes

Blend No.	Composition, wt% Cement LTS #14	Opal	Alkali[a] as Equivalent Na_2O, wt %: Starting blend	Amount found in paste after 14 years[c]	Amount leached from paste after 14 years	Alkali leached, % of alkali in starting blend	SiO_2[b] in blend wt %	Na_2O/SiO_2[c] Mole ratio in paste
14-1	100	0	0.93	0.14	0.79	85	22.60	0.0061
14-2	90	10	0.86	0.26	0.60	70	29.32	0.0086
14-3	83	17	0.80	0.68	0.12	15	34.02	0.0193
14-4	76.5	23.5	0.75	0.71	0.04	5	38.39	0.0180
		Shale						
14-6	87	13	1.08	0.48	0.60	56	28.16	0.0164
14-7	77	23	1.19	0.95	0.24	20	32.45	0.0283
14-8	69	31	1.28	1.16	0.12	9	35.87	0.0312
		Fly Ash						
14-10	83.5	16.5	1.26	0.49	0.77	61	26.84	0.0176
14-11	72	28	1.48	0.93	0.55	37	29.80	0.0300
14-12	63	37	1.66	1.05	0.61	37	32.12	0.0319
	Cement LTS #18	Opal						
18-1	100	0	0.21	0.07	0.14	67	21.72	0.0031
18-2	90	10	0.21	0.09	0.12	57	28.53	0.0032
18-3	83	17	0.20	0.24	-0.04[d]	-20	33.29	0.0071
18-4	76.5	23.5	0.20	0.26	-0.06[d]	-30	37.72	0.0067
		Shale						
18-6	87	13	0.45	0.21	0.24	53	27.40	0.0074
18-7	77	23	0.63	0.56	0.07	11	31.77	0.0170
18-8	69	31	0.78	0.76	0.02	3	35.27	0.0208
		Fly Ash						
18-10	83.5	16.5	0.66	0.07	0.59	89	26.11	0.0026
18-11	72	28	0.96	0.31	0.65	68	29.17	0.0102
18-12	63	37	1.20	0.54	0.66	55	31.56	0.0155

[a] Ignited basis
[b] Loss free
[c] After leaching
[d] Minus readings indicate no leaching, probably experimental error

Paste cylinders (2 in. diameter x 4 in. height) were made using a water/cement+pozzolan ratio of 0.5 by weight. These cylinders were cured for 1, 7, 28, 90 days and 14 years at 73^{o}F and 100% relative humidity. In order to perform various experiments, a portion of paste from each cylinder was sliced off, ground to pass through a 200 mesh sieve, and dried at 50% relative humidity. The amount of $Ca(OH)_2$ was determined by a Rigaku-Denki simultaneous differential and thermogravimetric analyzer (DTA/TGA). Alkalies (Na_2O and K_2O) were determined by a Perkin-Elmer atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Alkali Leached From Pastes

After curing for 14 years in a fog room, the pastes were analyzed for alkali content. Table 2 shows the amount of original alkali present, along with alkali present after 14 years curing. Alkali found in the pastes after curing is referred to as "alkali retained," i.e., alkali not leached from the pastes.

The amount of alkali leached out of the paste after curing for 14 years depended on the composition of the blend. As the amount of pozzolan in the blend increased, the amount of alkali leached from the paste generally decreased, irrespective of the pozzolan used. Graphical presentation of these data is given in Fig. 1 for blends made with cement LTS #14. A plot of the amount of alkali leached as a function of silica content shows a decrease in the amount of alkali leached with an increase in the pozzolan content of blends. The highest amount of alkali as leached from the portland cement paste, while the lowest was from the blend containing 23.5% opal. In other words, 95% of the total alkali present in the blend containing 23.5% ground opal was retained by the paste as compared to 15% in the portland cement paste (LTS #14). Mechanism of retention of alkali in blended cement paste has been previously discussed in detail.(2,3)

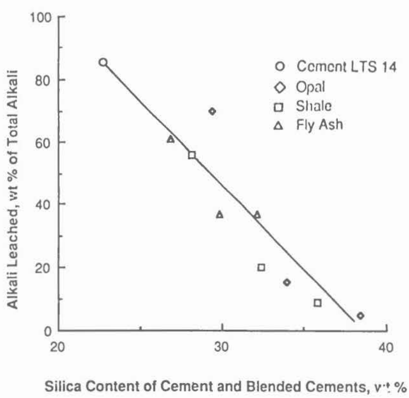

Figure 1. Alkali Leached from Portland Cement and Blended Cement Pastes Cured for 14 Years (numbers represent the amount of pozzolan in blends)

It was also observed that the amount of alkali leached was different for pastes prepared with different pozzolans, even though the blends had approximately the same C/S mole ratio. For example, for pozzolan blended cement pastes having C/S mole ratio of 1.40 ± 0.10 (the highest level for each of these pozzolans), the alkali leached in the order fly ash > shale > opal (Table 2). This trend was generally the same for other C/S mole ratio blended cement pastes. The reason for this trend became understandable when the C/S mole ratios of calcium silicate hydrate of individual blended cement pastes were calculated (Table 3, column 9), and plotted as a function of alkali retained (alkali not leached) in calcium silicate hydrates (Fig. 2).

Table 3. Determination of $Ca(OH)_2$ in 14 Year Cured Past Calculation of Various CaO/SiO_2 Mole Ratios

1	2	3	4	5	6	7	8	9	10
Blend No.	CaO in Silicates of cement, wt %	CaO in Pozzolan, wt %	CaO[a] wt %	$Ca(OH)_2$ in Paste, wt %	CaO in $Ca(OH)_2$ of Paste, wt %	CaO in CSH,[b] wt %	SiO_2 in Cement + Pozzolan wt	C/S Mole Ratio of CSH in Paste[c]	C/S Mole Ratio of Silicates in Cement + Pozzolan[d]
	Cement LTS #14	Opal							
14-1	53.41	0.00	53.41	26.99	20.43	32.98	22.6	1.55	2.52
14-2	48.07	0.04	48.11	15.84	11.99	36.12	29.3	1.31	1.76
14-3	44.33	0.07	44.40	7.15	5.41	38.99	34.0	1.23	1.39
14-4	40.86	0.10	40.96	3.03	2.29	38.67	38.3	1.08	1.14
		Shale							
14-6	46.47	1.45	47.92	16.52	12.50	35.42	28.1	1.34	1.81
14-7	41.13	2.56	43.69	9.29	7.03	36.66	32.4	1.20	1.44
14-8	36.85	3.46	40.31	4.77	3.61	36.70	35.8	1.08	1.20
		Fly Ash							
14-10	44.60	1.24	45.84	12.90	9.76	36.08	26.8	1.42	1.82
14-11	38.46	2.10	40.56	5.10	3.86	36.70	29.8	1.30	1.44
14-12	36.65	2.78	36.43	1.71	1.29	35.14	32.1	1.19	1.20
	Cement LTS #18	Opal							
18-1	52.40	0.00	52.40	29.44	22.28	30.12	21.7	1.50	2.58
18-2	47.16	0.04	47.20	13.94	10.55	36.65	28.5	1.38	1.79
18-3	43.49	0.07	43.56	8.93	6.76	36.80	33.2	1.20	1.42
18-4	40.09	0.10	40.19	1.91	1.45	38.74	37.7	1.10	1.14
		Shale							
18-6	45.59	1.45	47.04	17.82	13.49	33.55	27.4	1.30	1.83
18-7	40.35	2.56	42.91	10.66	8.07	34.84	31.7	1.17	1.45
18-8	36.16	3.46	39.62	6.04	4.57	35.05	35.2	1.07	1.20
		Fly Ash							
18-10	43.75	1.24	44.99	13.45	10.18	34.81	26.1	1.44	1.86
18-11	37.73	2.10	39.83	3.50	2.65	37.18	29.1	1.35	1.45
18-12	33.01	2.78	35.79	0.00	0.00	37.79	31.5	1.14	1.14

[a] (Column 2 plus Column 3)
[b] (Column 4 minus Column 6)
[c] (Column 7 divided by column 8 after converting to moles)
[d] (Column 4 divided by Column 8 after converting to moles)

It was assumed that all the alkali was retained by calcium silicate hydrate. The alkali retained was obtained by subtracting the leached alkali from total alkali. A straight line was fitted to the data between alkali retained and C/S mole ratio of calcium silicate hydrates. It was also observed that a small change in C/S mole ratio of calcium silicate hydrate can significantly influence alkali retention.

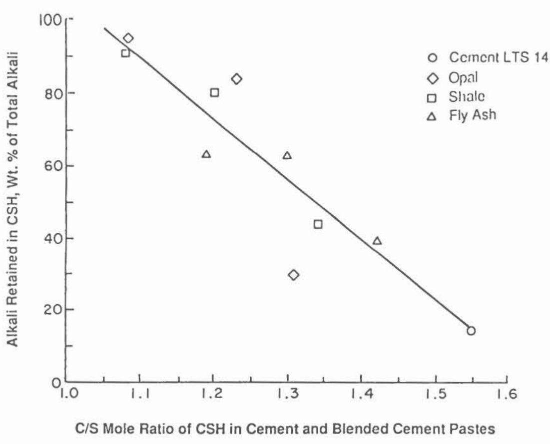

Figure 2. Alkali Retained in Calcium Silicate Hydrate formed in Portland Cement and Blended Cement Pastes.

Calcium Hydroxide and Alkali Content

An interesting relationship was found when $Ca(OH)_2$ content of portland cement paste (LTS #14) and of blended cement pastes was plotted as a function of alkali content of pastes after 14 years curing (Fig. 3). The amount of alkali retained in the paste increased with a decrease in $Ca(OH)_2$. This was due to the fact that $Ca(OH)_2$ reacted with pozzolan to form calcium silicate hydrate which retained more alkali.

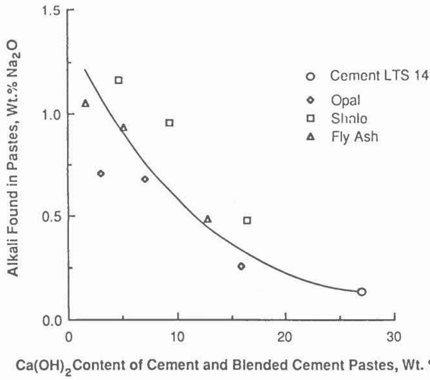

Figure 3. Relationship Between $Ca(OH)_2$ and Alkali in Portland Cement Pastes and Blended Cement Pastes

Calcium Hydroxide and Curing Time

Figs. 4 through 9 show a plots of $Ca(OH)_2$ produced in portland cement pastes and blended cement pastes cured up to 14 years. For both portland cements (LTS #14 and #18), the amount of $Ca(OH)_2$ appeared to reach a plateau between 90 days and 14 years. Irrespective of the pozzolan used, $Ca(OH)_2$ content of blended cement pastes reached a maximum and then decreased with time. In some cases, the maximum was quite pronounced.

The maximum is believed to represent the point in time after which more $Ca(OH)_2$ starts to react with pozzolan than the amount of $Ca(OH)_2$ being formed by the hydration of cement. It is suggested that the earlier (in time) this maximum occurs, the less will be the possibility of deleterious expansion because less alkali will be available for reaction with reactive siliceous aggregate. Therefore, more reactive pozzolan should be desirable.

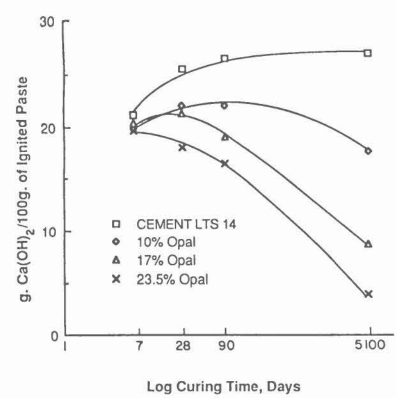

Figure 4. $Ca(OH)_2$ in Portland Cement Paste LTS #14 and Blended Cement Pastes containing Opal vs Curing Time up to 14 Years

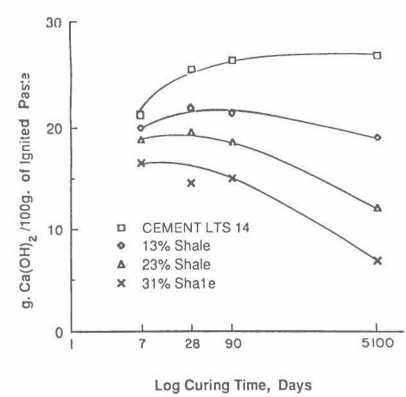

Figure 5. $Ca(OH)_2$ in Portland Cement Paste LTS #14 and Blended Cement Pastes containing Shale vs Curing Time up to 14 Years

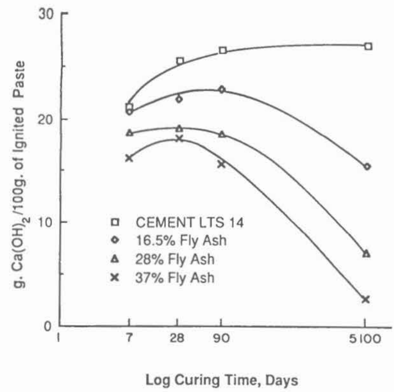

Figure 6. $Ca(OH)_2$ in Portland Cement Paste LTS #14 and Blended Cement Pastes containing Fly Ash vs Curing Time up to 14 Years

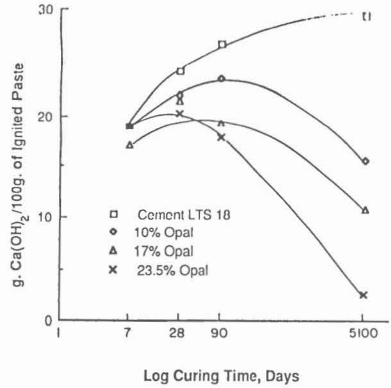

Figure 7. $Ca(OH)_2$ in Portland Cement Paste LTS #18 and Blended Cement Pastes containing Opal vs Curing Time up to 14 Years

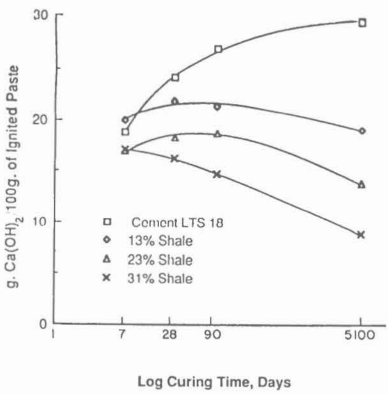

Figure 8. $Ca(OH)_2$ in Portland Cement Paste LTS #18 and Blended Cement Pastes containing Shale vs Curing Time up to 14 Years

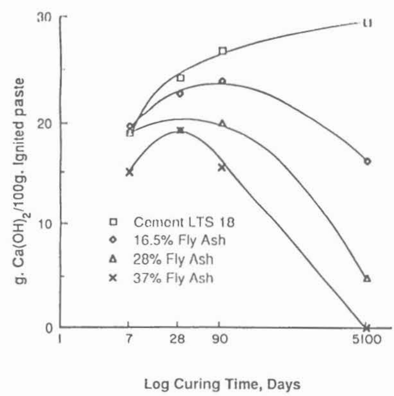

Figure 9. $Ca(OH)_2$ in Portland Cement Paste LTS #18 and Blended Cement Pastes containing Fly Ash vs Curing Time up to 14 Years

Pozzolan Requirement for Complete $Ca(OH)_2$ Reaction

Figs. 10 & 11 show the relationship between $Ca(OH)_2$ present in the paste after 14 years curing as a function of pozzolan content. It was assumed that both cement and pozzolan had reacted completely, although petrographic analyses had shown that unhydrated cement and unreacted pozzolan were still present in the pastes. Only DTA results of the blended cement paste prepared from the blend containing 63% cement LTS #18 and 37% fly ash did not show any $Ca(OH)_2$ in the paste.

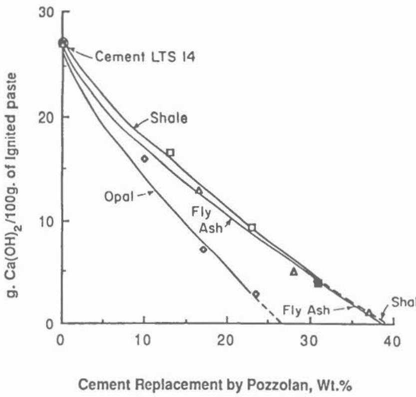

Figure 10. Reaction Between Pozzolan and $Ca(OH)_2$ Produced by Portland Cement LTS #14

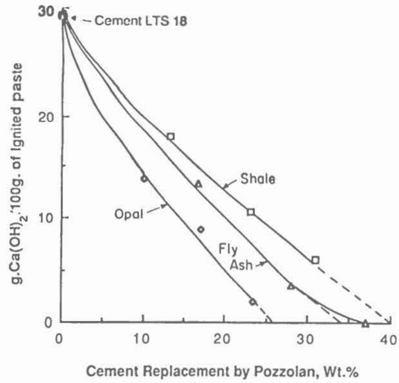

Figure 11. Reaction Between Pozzolan and $Ca(OH)_2$ Produced by Portland Cement LTS #18

Table 4 lists the amount of each pozzolan that will be needed for complete reaction of $Ca(OH)_2$ with pozzolan. These amounts were obtained by extrapolating the curves to the x-axis in Figs. 10 and 11. This extrapolation also showed that for blended cement paste made from the portland cement LTS #18 and fly ash, only 34% fly ash was needed for complete reaction with $Ca(OH)_2$ while the actual amount of ash added was 37%. For the same C/S mole ratio of blended cements, fly ash was the most effective reactor with $Ca(OH)_2$.

Table 4. Pozzolan Needed for Complete $Ca(OH)_2$ Reaction

Pozzolan	Amount Needed, wt% LTS #14	LTS #18
Opal	26	26
Shale	39	40
Fly Ash	38	34

It is known that replacement of portland cement with 25-30% of well performing Class F fly ash prevents alkali-aggregate reaction and since the alkali is immobilized at these levels of pozzolan, it is a fair assumption that the mechanics of alkali-aggregate reaction prevention stem from this immobilization.

Basicity of Cement and Alkali-Aggregate Expansion

Ming-Shu, et al., (1983) reported the relationship between basicity of various blended cements and alkali-aggregate reaction. They concluded that when the cements have the same alkali content, the lower the basicity of cement, the less vigorous is the alkali-silica reaction. The basicity was calculated using the ratio of basic oxides to acid oxides, i.e., $CaO/(SiO_2+Al_2O_3+Fe_2O_3)$. We believe that only the CaO content of silicates of cement and of pozzolan influences the basicity with respect to alkali-aggregate reactivity because lime content of silicates of cement and lime in pozzolans can produce $Ca(OH)_2$ on hydration. Other cement compounds such as C_3A and C_4AF do not produce $Ca(OH)_2$ when they react with water. A C/S mole ratio calculated from a combination of silicates of cement and pozzolan (Table 3, Column 10) would be more meaningful compared to the calculation of Ming-Shu, et al., (op cit.) which includes CaO from C_3A and C_4AF. Therefore, if the C/S mole ratio of blended cements is less than 1.5, deleterious expansion due to alkali-aggregate reaction can be reduced considerably to avoid cracking of concrete (Bhatty 1985). The ratio may be increased or decreased by adjusting the amount of pozzolan. Further studies should be undertaken to establish a relationship between C/S mole ratio and the amount of alkali that will not cause any deleterious expansion. When this is known, the C/S mole ratio of blended cement can be adjusted, depending upon the amount of alkali present.

The C/S mole ratio of calcium silicate hydrate formed in portland cement pastes and blended cement pastes was also calculated (Table 3, Column 9) assuming that all the silica of pozzolan had reacted. Previous studies (Bhatty & Greening 1978) indicated that recycling of alkali starts when C/S mole ratio of calcium silicate hydrate is about 1.32, but no recycling was observed when C/S mole ratio was 1.25 or less. Therefore, when the C/S mole ratio of calcium silicate hydrate in blended cement is 1.25 or less, a decrease in alkali-aggregate reaction would be expected and this decrease could continue as the C/S mole ratio decreases further, presumably to 1.

SUMMARY AND CONCLUSIONS

Long term hydration and exposure to moisture of blended cements made from high alkali portland cement and pozzolans has shown that as much as 95% of the total alkali can be retained in the blended cement paste compared to only 15% of total alkali in portland cement paste. The amount of alkali retained in the paste depends on the nature and amount of pozzolan used in the blend. It can be concluded that the lower the amount of leachable alkali from the paste, the less likely the deleterious expansion of concrete or longer the delay in deleterious expansion if insufficient pozzolan is present. In other words, more alkali tied up in the calcium silicate hydrate produces a more stable system with respect to deleterious alkali-aggregate reaction.

The amount of alkali retained in blended cement pastes increased as the amount of calcium hydroxide decreased. The decrease in the amount of calcium hydroxide resulted from the reaction with pozzolan and subsequent formation of calcium silicate hydrate. It was also possible to determine the amount of pozzolan required to completely react with the calcium hydroxide produced by the hydration of cement. Further studies to use this approach as a possible method of determining pozzolan requirements should be investigated. This might require a faster hydration procedure using a high water-cement ratio.

Methods of calculation of the C/S mole ratio of blended systems are presented and the relationship between C/S mole ratio and alkali-aggregate expansion is discussed.

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