

EFFECT OF CEMENT COMPOSITION ON EXPANSION OF MORTAR BARS
DUE TO ALKALI-SILICA REACTION

Hung Chen* and P.E. Grattan-Bellew**

* Lafarge Canada Inc, 6150 Royalmount, Montreal, QC
Canada, H4P 2R3

** Institute for Research in Construction
National Research Council, Bldg. M 20, Ottawa, ONT, Canada K1A 0R6

1. INTRODUCTION:

The role of different phases of portland cements on the expansion of mortar bars made with alkali reactive aggregates is not understood. In earlier research reported by Stanton [1], and others [2,3], the effect of phase composition was investigated, but due to the number of variables in the commercial cements, it was only possible to determine the effect of alkalis on expansion. In some recent research [4], it was shown that the alkalis present in the sulfate phases in the clinker caused the most expansion of mortar bars, while alkalis occurring in the calcium silicate phases has the least effect on expansion. It has also been suggested that Ca(OH)_2 in concrete has a negative role in alkali-aggregate reaction [5,6,7] and it was thought that the high C_3S levels in modern cements may contribute to higher levels of Ca(OH)_2 in concrete and hence to a lower durability vis a vis alkali-aggregate reactivity; the validity of this hypothesis has not been demonstrated.

In the present study, a suite of cements were made under carefully controlled laboratory conditions so that the effects of changes in the C_3A , C_3S and alkali contents of the cements on expansion due to alkali-aggregate reaction, could be studied independently.

2. EXPERIMENTAL

2.1. Preparation of cements

The raw materials used in the production of the laboratory cements were obtained from the Woodstock plant of Lafarge Canada Inc. K_2SO_4 and Na_2SO_4 were added, when necessary, to the raw feed prior to firing to provide additional alkali [8]. A small quantity of water was added to each raw mix which was then pressed into pellets, dried at 150°C , calcined for 30 minutes at 950°C , and then fired at 1450°C for 30 minutes; this was followed by rapid cooling in air to ambient temperature. In all 17 cements were made. The burning time at 1450°C for 7 clinkers #111, #121, #122, #131, #132, #211 and #212 was increased to 40 minutes to reduce the alkali to the intended levels. The cements were made by intergrinding the clinkers with optimum amount of gypsum, to a fineness of $370 \text{ M}^2/\text{kg}$. The final alkali contents of cements #112, #212 and #222 were adjusted to the desired level by the addition of 0.28%, 0.14% and 0.56% K_2SO_4 , respectively.

2.2. Preparation and storage of mortar bars:

The mortar bars were prepared according to the specifications in ASTM C227 [9] except that the w/c ratio was fixed at 0.485. A well documented siliceous limestone was used as reactive aggregate [10]. Following demoulding, the mortar bars were precured for one day under one of two conditions: i. at 23°C and 100% humidity, ii. two hours in a moist curing cabinet at 23°C followed by 8 hours at 70°C and 100% humidity and finally, 14 hours at 23°C and 100% humidity, referred to subsequently as 70°C precuring. The first length measurement was made at the end of the precuring period. After the initial measurement the mortar bars were stored at 38°C and 100% humidity. Length change of the mortar bars was monitored for two years. One bar from each set was removed after six months of storage and the amount of Ca(OH)₂ and ettringite in them was determined.

3. COMPOSITIONAL EFFECTS

3.1.1. Cement composition:

The chemical composition of the cements is shown in table 1. The phase compositions of the clinkers determined by the Bogue calculation and by point counting with an optical microscope is shown in table 2.

Table 1. Chemical composition of cements.

CEMENT #	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	CaO %	MgO %	Na ₂ O %	K ₂ O %	Na ₂ O .Na ₂ O eqv.% sol. %	SO ₃ %	LOI %	
*1								*2			
111	19.7	5.19	1.45	61.12	3.06	0.41	1.14	1.16	0.77	4.12	1.34
112	20.3	3.76	3.71	60.95	3.28	0.47	1.09	1.19	0.48	3.08	1.23
121	20.4	5.15	1.50	62.06	3.13	0.42	1.22	1.22	0.77	4.39	1.45
122	21.0	3.83	3.74	61.07	3.35	0.50	0.99	1.15	0.39	3.03	1.20
131	20.9	5.17	1.52	61.08	3.14	0.44	1.26	1.27	0.71	3.60	1.59
132	21.7	3.89	3.65	61.07	3.40	0.51	1.03	1.19	0.40	3.19	1.25
211	20.4	5.50	1.52	65.3	2.71	0.43	0.73	0.91	0.41	3.71	1.36
212	20.5	3.93	3.87	62.96	2.86	0.43	0.73	0.91	0.43	2.72	0.97
221	20.4	5.27	1.43	62.84	2.61	0.44	0.65	0.87	0.25	4.28	1.78
222	21.5	3.95	3.86	62.86	2.69	0.36	0.84	0.91	0.38	2.7	0.84
231	21.6	5.33	1.45	62.47	2.64	0.38	0.77	0.89	0.41	3.68	1.36
232	22.3	3.86	3.76	62.13	2.72	0.49	0.68	0.94	0.24	2.71	1.10
13	20.8	4.56	2.64	62.57	3.95	0.18	0.97	0.81	0.45	2.93	1.80
14	20.8	4.56	2.72	62.48	3.96	0.19	0.97	0.83	0.46	2.89	1.62
15	20.1	6.23	3.95	63.19	1.11	0.14	0.64	0.56	0.39	2.85	1.09
16	19.7	6.07	3.81	64.27	1.03	0.13	0.69	0.58	0.43	3.05	1.19
17	20.6	6.25	4.01	63.75	1.07	0.13	0.59	0.52	0.48	2.79	0.93

- *1. Composition of cements is indicated by a three digit code: The first digit indicates the alkali content of the cement, the second C₃S content and the third the C₃A content.
- *2. Soluble alkali determined after 1 minute in water. Cements 11-17 were ground from commercial clinker.

3.1.1.2. Mortar bar expansions:

The expansion of mortar bars made with high alkali cements (1.20±0.05%) is shown in figure 1; it is evident that high alkali cements with high C₃A contents gave rise to the greatest expansion of mortar bars. There is no clear

differentiation between the rates of expansion of mortar bars made with medium alkali cements with high and low C₃A contents, however, alkali in the form of K₂SO₄ was added to low C₃A cements #212 and #222 resulting in an increase their expansion potential and a distortion of the relationship between it and the C₃A content of cement.

The five cements made from commercial clinker all have low C₃A contents; expansions of mortar bars made with these cements were proportional to their alkali contents.

Table 2. Phase composition of laboratory made cements determined by Bogue calculation and by optical optical microscopy.

CEMENT #	BOGUE POTENTIAL COMPOUNDS				PHASE COMPOSITION BY MICROSCOPY					
	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	CaO	MgO
#	%	%	%	%	%	%	%	%	%	%
111	59.415	612.14	7	54	28	11.5	3.4	1.1	2.2	
112	61.215	73.9	12.1	52	30	3.7	13.8	1.2	2.2	
121	49.025	812.04	9	41	40	10.6	4.7	1.7	1.8	
122	51.525	34.0	12.1	50	27	5.4	16.8	0.6	2.0	
131	40.134	412.15	0	39	38	13.3	8.3	0.3	0.8	
132	40.235	94.4	11.8	48	34	2.0	16.2	0.2	0.6	
211	59.216	612.64	8	76	8	14.7	0.8	0.3	0.8	
212	59.117	04.1	12.4	61	15	3.8	16	2.0	2.2	
221	50.3	26	12.64	8	61	23	13.4	1.0	0.0	1.4
222	50.527	04.2	12.4	57	26	2.5	13.3	0.5	1.0	
231	39.736	312.54	7	52	33	13.1	1.2	0.2	0.8	
232	40.636	94.1	12.1	50	30	3.6	14.9	0.1	2.1	
13	50.724	27.9	8.3	61	21	4.0	11.5	0.8	2.2	
14	51.623	57.8	9.6	62	13	5.7	18.9	0.0	0.5	
15	51.520	310.1	12.3	44	35	2.8	17.7	1.0	0.0	
16	58.513	89.9	11.9	58	22	3.5	16.2	0.7	0.0	
17	50.322	510.0	12.5	37	40	3.4	18.1	0.7	0.0	

*1. Composition of laboratory made cements is indicated by a three digit code: The first digit indicates the alkali content of the cement, the second, its C₃S content and the third, its C₃A content. Cements # 13-17 were ground from commercial clinker.

3.1.2. Determination of rates of expansion of mortar bars:

The rates of expansion of the mortar bars were calculated after the method of Grattan-Bellew [11]. Rates of expansion were used to investigate correlations between the expansion of mortar bars and the different phases in the cements. Data for the 17 cements show that there is excellent correlation between the rates of expansion and the expansions of mortar bars at all ages. (correlation coefficients were in the range of 0.95-0.98)

3.1.3. Correlation between rates of expansion of mortar bars and the composition of the cements:

Multiple regression analysis was used to investigate correlations between the different phases of the cements or combinations of them and the rates of expansion of mortar bars; only the total acid soluble alkali contents correlated with expansions. The rates of expansion of all the mortar bars precured at 23°C and cured at 38°C were plotted against the alkali contents of

the cements in figure 2, from which it can be seen that there is only moderately good correlation between the rates of expansion and the alkali content of the cements. The rates of expansion for the high alkali cements ($1.197 \pm 0.05\%$ Na_2O eqv.) vary between 18.7×10^{-3} and $30.1 \times 10^{-3} \text{ days}^{-1/2}$ with a mean value of $23 \pm 8 \times 10^{-3} \text{ days}^{-1/2}$. As the expected variation due to differences in expansion within a set of mortar bars is 8% i.e. $\pm 2 \times 10^{-3} \text{ days}^{-1/2}$, for the above set, factors other than the alkali content of the cements probably account for the spread in the rates of expansion observed in figure 2. It is evident from figure 1 that the expansion of mortar bars is influenced by the C_3A content of the cements.

It was thought that the crystallization of ettringite in cracks and air voids might be contributing to the late stages of expansion of the mortar bars, thus giving rise to the spread in the rates of expansion of the mortar bars made with the high alkali cements which contain the most soluble sulfates and hence have the greatest potential for ettringite formation. No correlation was found between the rates of expansion of mortar bars made with cements #111, #112, #121, #122, #131, and #131, and the amount of ettringite in the mortar bars after 6 months.

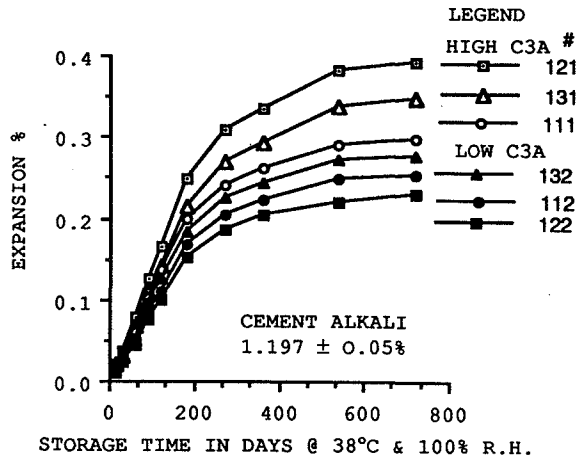


Figure 1. Effect of C_3A content of cement on expansion of mortar bars made with high alkali cement.

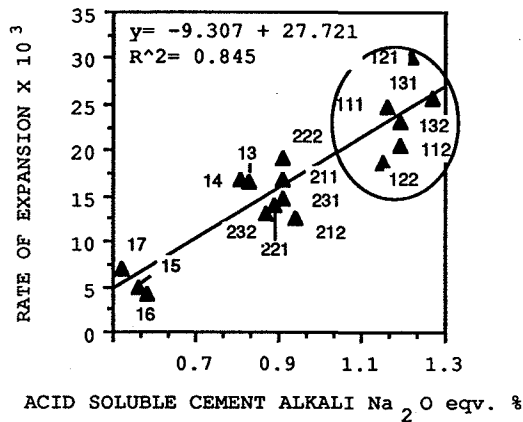


Figure 2. Effect of alkali content of cement on expansion of mortar bars.

3.1.4. Effect of percentage of $(\text{C}_3\text{A} + \text{SO}_3)$ in cements on the ettringite content of mortar bars:

Correlation between the $(\text{C}_3\text{A} + \text{SO}_3)$ content of the cements and the ettringite content of mortar bars after six months is relatively poor, but, as would be expected, the ettringite content of mortar bars made with high C_3A cements is higher than those made with low C_3A cements.

3.1.5. Effect of soluble alkali content of cements on expansion:

The soluble alkali contents of the cements were determined by one minute extraction in water at 23°C. One minute extraction was used as it has been shown that alkalis dissolved in one minute are those present in the sulfate phases in the cement [4] Alkalis present in sulfate phases are thought to contribute most to the expansion of mortar bars containing reactive aggregates. No correlation was found between the rates of expansion of mortar bars made with all cements and the soluble alkali content of the cements. However, when the cements made from commercial clinker, numbers 13-17, for which there is no correlation between rates of expansion and soluble alkali, were excluded, a moderate correlation was found. In the second author's experience with Canadian cements, better correlation is usually obtained with total alkali rather than soluble alkalis and the rates of expansion of mortar bars or concrete prisms.

3.1.6. Effect of C₃S content of cement on calcium hydroxide content of mortar bars

No correlation was found between the C₃S content of the cements and the calcium hydroxide content of the mortar bars after 6 months storage at 38°C and 100% humidity, when all the cements were included. But when the cements made from plant clinker are excluded a moderate correlation was found between the C₃S content of the cement and the calcium hydroxide content of the mortar, (the correlation coefficient was 0.716) Because calcium hydroxide is thought to be necessary for the occurrence of deleterious alkali aggregate reactivity [5] it has been assumed that modern high strength cements with high C₃S levels result in poor durability of concrete made with potentially reactive aggregates. The results of the present study show that for a variation of 37% in the C₃S content of the cements there was only a 2% change in the amount of calcium hydroxide in the mortar; this would have a negligible effect on expansion due to alkali-aggregate reaction.

4. CONCLUSIONS

- i. This study has confirmed that the total acid soluble alkali content is the only component which significantly effects the expansion of mortar bars made with reactive siliceous limestone aggregate.
- ii. Mortar bars made with high alkali cements (1.19% Na₂O eqv.) containing high levels of C₃A (12.8±2.2%), showed greater expansions than those with low levels of C₃A (3.7±1.7%) although no direct correlation was found between the C₃A content of the cement and the expansion of mortar bars.
- iii. No correlation was found between the ettringite content of the mortar bars and their expansion.

ACKNOWLEDGEMENTS:

The first author gratefully acknowledges a research contract NO. 14SQ. 31944-0032 from Supply and Services Canada, which made this research possible. Both authors also acknowledge the support of the Cement-Aggregate Sub-Committee CSA-A5 of the Canadian Standards Association.

5. REFERENCES

- [1] Stanton, T.E. Expansion of Concrete Through Reaction Between Cement and Aggregate. American Soc. of Civil Engineers, Papers, Dec. 1940, 1781-1811
- [2] Bailey, T. The Effect of Alkalies in Portland Cement on the Durability of Concrete. Journal of American Concrete Inst., 16, 2, 89-104, 1944.
- [3] Conrow, A.D., Cement-Aggregate-reaction Expansion of Concretes Containing Kaw River Sand-gravel as Aggregate when Made with a Representative Range of Portland Cements Manufactured in the Central United States Region, Unpublished Report of Ash Grove Lime Portland Cement Company, Chanute, Kansas 1950.
- [4] Struble, L., and Diamond, S., Influence of Cement Alkali Distribution on Expansion Due to Alkali-Silica Reaction, ASTM STP 930, Alkalies in Concrete, Ed. Dodson V.H. Los Angeles, Calif., 25 June 1985, 31-45.
- [5] Chatterji, S., The Role of $\text{Ca}(\text{OH})_2$ in the Breakdown of Portland Cement Concrete due to Alkali-Silica Reaction, Cement. Concr. Res., 9, 185, 1979.
- [6] Tang, M.S. and Han, S.F., Effect of Calcium Hydroxide on Alkali Silica Reaction, Proc. 7th Intern. Congr. on Cem. Chem., Paris, 1980, II., 94.
- [7] Kichitani, K. I., and I, Sk., Influence of $\text{Ca}(\text{OH})_2$ on Alkali-Silica Reaction, Semento Gijitsu Nempo, 38, 102, 1984.
- [8] Hung Chen, The Effect of Cement Composition on Alkali-Aggregate Reaction Final Report, DSS Contract No. 1SQ84-00349, August 1988, Institute for Research in Construction, National Research Council, Ottawa, Canada.
- [9] ASTM C227-87 Standard Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar Bar Method), 1988 Annual Book of ASTM Standards, Section 4, Construction, Concrete and Aggregates. ASTM 1916 Race Street, Philadelphia, USA., 121-125.
- [10] Rogers, C. A., General Information on Standard Alkali-Reactive Aggregates from Ontario, Canada., p.59, Engineering Materials Office, Ministry of Transportation, 1203 Wilson Avenue, Downsview, Ontario, Canada. (Undated)
- [11] Grattan-Bellew, P.E., A Review of test Methods for Alkali-Expansivity of Concrete Aggregates, Proc. of 5th International Conf. on Alkali-Aggregate Reaction in Concrete, Cape Town, 1981, S252/9.