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Interrelations Between Cement and Concrete Properties, Part 2

Sulfate Expansion, Heat of Hydration, and Autoclave Expansion

R. L. Blaine, H. T. Arni, and D. N. Evans

Building Research Division
Institute for Applied Technology
National Bureau of Standards
Washington, D.C.

Building Science Series 5

Issued July 1, 1966

For sale by the Superintendent of Documents, U.S. Government Printing Office
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Contents

Section 4. Variables Associated with Expansion in the Potential Sulfate Expansion Test

R. L. Blaine, H. T. Arni, and D. N. Evans

The relationships between the chemical characteristics of 183 portland cements and the expansion of mortar bars made of one part cement with 7.0 percent SO_3 and 2.75 parts graded Ottawa sand were studied by computing multivariable regression equations with the aid of a digital computer and determining which of the independent variables had a significant effect on the expansion values. For cements containing 0 to 9 percent C_3A, a linear relationship appeared adequate whereas a higher power of the C_3A content was required with cements having 7 to 15 percent C_3A. The principal variables other than the potential C_3A content associated with the expansion were the Fe_2O_3 content and CaO/SiO_2 ratio. Of the other commonly determined variables, the loss on ignition, insoluble residue and K_2O content were associated with high expansion values of the low C_3A cements. Certain minor constituents or trace elements such as SrO, Cu, Cr, Ni, P, V, and Zn also appeared to be associated with the expansion values of the cements. The use of the potential C_3S content or the compressive strength of mortar cubes as variables indicated that high C_3S was associated with cements having low expansion values as determined by this test.

CONTENTS

1. Introduction

The ability of portland cement concretes to withstand the destructive action of waters or soils containing alkaline sulfates has been the subject of many investigations, and there is extensive literature on the subject [1, 2, 3, 4].[1] The studies have been made under both laboratory and field conditions, many of these in the development of test methods and specifications to assure satisfactory performance of concretes exposed to severe or moderate sulfate action [5].

Although it is recognized that the cement content, water-cement ratio, and quality of the aggregate used in the concrete, as well as the curing, are important factors in determining the sulfate durability, it is also recognized that the cement composition, especially the potential tricalcium aluminate content of the cement, is one of the major factors associated with the durability of the concrete under these conditions. However, it has been reported that [6] "We must look elsewhere than to the aluminate for an explanation of the vulnerability of concrete to sulfate solutions," and [7] "There is some unrecognized factor in cement which affects the sulfate resistance."

For lack of a satisfactory performance test yielding reproducible, definitive results within a reasonable time, it has been necessary in both Federal [8] and ASTM [9] specifications to impose certain chemical limitations on the cements intended for use where sulfate resistance is a factor. Since these specification limits were first adopted, a number of revisions have been made. In 1955 the Working Committee on Sulfate Resistance of ASTM Committee C–1 proposed a "Performance Test for the Potential Sulfate Resistance of Port-

[1] Figures in brackets indicate the literative references at the end of this section.

land Cements" [5]. One of the conclusions of the report was "There is a relatively good relationship between the 28-day expansion of the mortar prisms and the performance of concretes exposed to sulfate soils." It was also indicated, among other things, that the proposed test method gave reproducible results which would discriminate between different cements. This test procedure, therefore, seemed to afford a means for determining some of the variables associated with sulfate durability. Tests were therefore made on a number of the cements which have previously been described [10, 11, 12], in an attempt to better determine the variables associated with the expansions caused by sulfates as determined by the proposed test method for potential sulfate expansion. In view of previously quoted statements in this section [6, 7] relative to the inadequacy of the explanation of the sulfate expansion solely in terms of pure compounds, consideration will be given to the possible effect of the minor and trace elements present in portland cements.

2. Materials

The frequency distributions of results of chemical analyses as well as spectrochemical analyses of the portland cements used in the study have previously been reported in part 1 of this series of articles [10, 11, 12] dealing with materials and techniques employed and the occurrence of minor and trace elements in portland cements. The test for potential sulfate expansion was made on 183 portland cements. These cements are believed fairly representative of the portland cements of the different types manufactured in the United States.

3. Testing Procedures

The testing procedures used followed closely (with a few exceptions as will be noted later) the recommendations of the Working Committee on Sulfate Resistance of ASTM Committee C-1 on Cement and the proposed method of test as originally published [5]. This method consisted of adding sufficient gaging plaster to the cement to make the SO_3 content 7.0 percent by weight of the cement. The 1:2.75 (cement-plaster to graded Ottawa sand) mortar was mixed in a mechanical mixer with the required amount of water.[2]

The plastic mortar was molded into $1\times1\times10$ inch effective-gage-length prisms and cured in a moist cabinet at 95–100 percent relative humidity for 24 hours, after which the molds were stripped and the length of the prisms measured. The specimens were stored in water and length measurements were made at 7, 14, 21, 28, 56, and 84 days from the time of molding. Additional measurements were made at monthly intervals for 1 year on specimens which had not warped, disintegrated, or been accidentally broken in handling. The testing procedure used deviated from the proposed testing procedures in that only three instead of six speciments were molded for each of the cements. The reduced number was possible because a special plastic tape was used to line the molds which facilitated the release of the specimens and reduced breakage. The expansion values expressed as a percentage increase in length based on the 24-hour measurements were the averages of the three specimens. However, when only two specimens remained intact after removal from the molds, their average expansion was used in future calculations. All specimens were made by one operator in one laboratory.

Supplementary tests on 21 portland cements (not included in the original series) were made using duplicate sets of three specimens on different days to evaluate the precision of the test results.

4. Statistical Treatment

The statistical treatment of the data used has been described in detail in a previous article [10]. Plots were made of the expansion values at 14, 28, and 84 days versus various independent variables, and equations were computed with different combinations of independent variables in order to find those combinations which resulted in the best fit attainable of the data to the computed relationship. The various exploratory techniques described in part 1, section 1 were used to determine which of the available independent variables should be tried in the equations and those independent variables which had "coefficient/s.d."[3] values less than one were deleted from computa-

[2] The combined proportions of dry materials mixed at one time consisted of 400 g of cement and gypsum molding plaster combined and 1100 g of graded standard sand. The quantity of mixing water used was as follows:

For types I, II, IV, and V cements	216 ml
For types IA and IIA cements	208 ml
For type III cement	224 ml
For type IIIA cement	216 ml

(The present requirement that an amount of water shall be used such that the mortar shall have a flow of 100 to 115 percent was not in effect at the time these tests were made.)

[3] The following statistical terms are used in this section:
S.D.=Estimated standard deviation calculated from the deviations from the fitted equation, or the estimated standard deviation of a single observed value of a variable.
s.d.=Estimated standard deviation of the coefficient of an individual independent variable used in a fitted equation.
Coef./s.d. or coefficient/s.d.=ratio of the estimated coefficient (of an independent variable used in an equation) to its estimated standard deviation.
"F"=Fisher's ratio of variances. Critical "F" values were obtained from tables presented in textbooks on statistics.
A more complete discussion is presented in the first section on "Materials and Techniques".

tions of subsequent equations. As in the previous article [11] both commonly determined variables and the minor constituents were employed in order to determine their possible effect. A discussion of the limitations of the statistical treatment has previously been presented [10].

5. Treatment of Data

The maximum specification limits of 5- and 8-percent tricalcium aluminate (C_3A)[4] for sulfate-resisting and moderate-sulfate resisting cements, respectively, have been in effect since the time of the development of specifications for the five types of portland cement (1930–1940). There have been some uncertainties with respect to these limits. Plots of sulfate expansion versus C_3A have, for example, generally indicated a "break" in the curve in the 7- to 9-percent C_3A region. This was also true in the present study, but there was no obvious corresponding break at the 5 percent C_3A specification limit. It therefore appeared desirable to combine the sulfate-resisting and moderate-sulfate-resisting cements into one group and include also those cements having up to 9.0 percent C_3A. For cements which were not classified as sulfate resisting it appeared desirable (because of the uncertainty of the value differentiating the cements with respect to moderate sulfate resistance) to include cements having 7 to 15 percent C_3A in a second group. Separate calculations were made on each of the two overlapping groups of cements with 0 to 9 and 7 to 15 percent C_3A, respectively. There were so few cements below the 5-percent specification limit for sulfate-resisting cements that equations developed for these cements alone would have been of no significance.

Although the expansion measurements were made at regular intervals up to one year, it appeared from plots of expansion versus age that the resulting lines for the different cements did not cross each other to any great extent at the early ages. Therefore computations were made for the expansion values only at 14, 28, and 84 days.

The nomenclature and abbreviations used in the previous section [10] are also used in this section. In addition, SE_{14}, SE_{28}, and SE_{84} are used to indicate the percentage expansion of the prisms at 14, 28, and 84 days, respectively.

6. Results of Tests

6.1. Results of Preliminary Examination

The frequency distributions of the cements with respect to expansion of the prisms at 14, 28, and 84 days are presented in tables 4–1, 4–2, and 4–3, respectively. It may be noted that with each of the types of cements, as classified, a considerable range of expansion values was obtained. Cements classified as types I and IA had the greatest range of values at all ages, and their ranges overlapped the ranges of values obtained with cements classified as types II, III, IV, and V [8, 9]. The cements

TABLE 4–1. *Frequency distribution of cements with respect to expansion of prisms in the potential-sulfate-expansion test*

Type cement	Percentage expansion at 14 days									Total
	0 to 0.020	0.020 to 0.040	0.040 to 0.060	0.060 to 0.080	0.080 to 0.100	0.100 to 0.120	0.120 to 0.140	0.140 to 0.160	0.160 to 0.180	
	Number of cements									
I	----	13	35	16	4	4	1	1	1	75
IA	----	1	2	3	1	1	----	----	----	8
II*	5	9	1	1	----	----	----	----	----	16
IIA*	----	1	----	----	----	----	----	----	----	1
II	1	41	6	----	----	----	----	----	----	48
IIA	----	1	----	----	----	----	----	----	----	1
III	1	10	5	2	----	----	----	----	----	18
IIIA	----	----	----	1	----	----	----	----	----	1
IV, V	4	9	2	----	----	----	----	----	----	15
Total	11	85	51	23	5	5	1	1	1	183

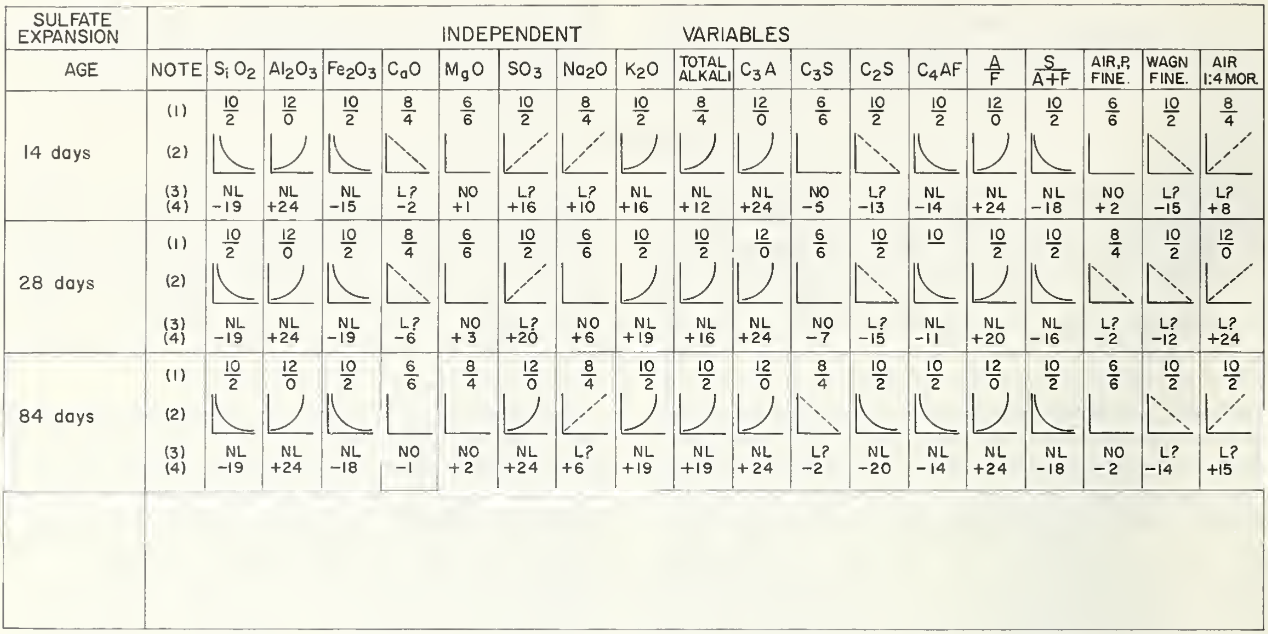
*Classified as type I and IA when procured.

TABLE 4–2. *Frequency distribution of cements with respect to expansion of prisms in the potential-sulfate-expansion test*

Type cement	Percentage expansion at 28 days												Total
	0 to 0.020	0.020 to 0.040	0.040 to 0.060	0.060 to 0.080	0.080 to 0.100	0.100 to 0.120	0.120 to 0.140	0.140 to 0.160	0.160 to 0.180	0.180 to 0.200	0.200 to 0.250	0.250 to 0.300	
	Number of cements												
I	----	3	11	24	13	10	3	4	3	1	1	2	75
IA	----	----	2	1	3	1	----	----	----	1	----	----	8
II*	2	9	4	----	----	----	----	1	----	----	----	----	16
IIA*	----	----	1	----	----	----	----	----	----	----	----	----	1
II	----	21	24	3	----	----	----	----	----	----	----	----	48
IIA	----	----	1	----	----	----	----	----	----	----	----	----	1
III	----	9	2	3	3	1	----	----	----	----	----	----	18
IIIA	----	----	----	----	----	1	----	----	----	----	----	----	1
IV, V	----	13	2	----	----	----	----	----	----	----	----	----	15
Total	2	55	47	31	19	13	3	5	3	2	1	2	183

*Classified as type I and IA when procured.

[4] The nomenclature customary in cement technology, viz, C_3A, C_3S, C_2S, and C_4AF, refers to the potential compound composition, tricalcium aluminate, tricalcium silicate, dicalcium silicate, and tetracalcium aluminoferrite, respectively, as calculated by standard procedures presented in both Federal and ASTM specifications for portland cements. The letters C, A, F, and S may sometimes be used in referring to CaO, Al_2O_3, Fe_2O_3, and SiO_2, respectively, as in the ratios A/F and S/(A+F) and C/S. In the C/S ratio, the CaO was corrected for the amount of CaO combined with the SO_3.
Other abbreviations include NAE for non-air-entraining cements, AE for air-entraining and AE+NAE for air-entraining plus non-air-entraining cements, APF or Air P. Fine, for fineness in square centimeters per gram as determined by the air permeability method, and Wagn. or Wagn. Fine. for fineness in square centimeters per gram as determined by the Wagner turbidimeter method. Also used were Loss for loss on ignition, Insol. for insoluble residue, and Alk for total alkali expressed in terms of percent Na_2O. (Total alkali = %Na_2O + 0.658% K_2O.) The values were determined by standard procedures.



SULFATE EXPANSION AGE	NOTE	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TOTAL ALKALI	C_3A	C_3S	C_2S	C_4AF	$\frac{A}{F}$	$\frac{S}{A+F}$	AIR,P. FINE.	WAGN FINE.	AIR 1:4 MOR.
14 days	(1)	10/2	12/0	10/2	8/4	6/6	10/2	8/4	10/2	8/4	12/0	6/6	10/2	10/2	12/0	10/2	6/6	10/2	8/4
	(2)																		
	(3)	NL	NL	NL	L?	NO	L?	L?	NL	NL	NL	NO	L?	NL	NL	NL	NO	L?	L?
	(4)	−19	+24	−15	−2	+1	+16	+10	+16	+12	+24	−5	−13	−14	+24	−18	+2	−15	+8
28 days	(1)	10/2	12/0	10/2	8/4	6/6	10/2	6/6	10/2	10/2	12/0	6/6	10/2	10	10/2	10/2	8/4	10/2	12/0
	(2)																		
	(3)	NL	NL	NL	L?	NO	L?	NO	NL	NL	NL	NO	L?	NL	NL	NL	L?	L?	L?
	(4)	−19	+24	−19	−6	+3	+20	+6	+19	+16	+24	−7	−15	−11	+20	−16	−2	−12	+24
84 days	(1)	10/2	12/0	10/2	6/6	8/4	12/0	8/4	10/2	10/2	12/0	8/4	10/2	10/2	12/0	10/2	6/6	10/2	10/2
	(2)																		
	(3)	NL	NL	NL	NO	NO	NL	L?	NL	NL	NL	L?	NL	NL	NL	NL	NO	L?	L?
	(4)	−19	+24	−18	−1	+2	+24	+6	+19	+19	+24	−2	−20	−14	+24	−18	−2	−14	+15

FIGURE 4–1. *Results of plotting sulfate expansion on the "Y" axis versus independent variables on the "X" axis.*
(1) Ratio of number of plotted points occurring in parts of diametrically opposite quadrants. (High ratios indicate significant relationships).
(2) General trend of line drawn through plotted points.
(3) Apparent nature of relationship, L=linear, NL=non linear, NO=no apparent relation, N?=nature of relationship not determinable.
(4) Quadrant sum. (absolute value of 11 or greater indicates a relationship at the 95% probability level. See ref. 10).

formerly classified as types I or IA but later classified as type II or IIA in the revised specification had, with one exception, expansion values in the same range as cements classified as type II in the earlier specifications. Most of the cements classified as type III had low expansion values at 14 days, but at 28 and 84 days the values of the different cements of this type were more widely scattered, and at 84 days two of them exceeded the median for type I cements.

In figure 4–1 are presented the results of plotting the expansion of the prisms at 14, 28, and 84 days on the y axis versus various independent variables on the x axis. The ratios in lines (1) and the numbers in lines (4) of the figure are the result of two methods of checking for random scatter of plotted points. A high ratio in line (1) indicates a high degree of correlation, or lack of randomness. In line (4) a quadrant sum with an absolute magnitude equal to or greater than 11 (24 is the maximum possible) indicates a significant relationship at the 95 percent probability level. The method of obtaining these figures and their meaning are described more fully in part 1 [10]. High values for Al_2O_3, C_3A, and A/F ratio were associated with those cements having high expansion values. To a lesser degree, the higher values for total alkali, K_2O, SO_3, and the air content of the 1:4 mortars also appeared to be associated with those cements having high expansion. It may also be noted that high values for SiO_2, Fe_2O_3, C_4AF, C_2S, S/(A+F), and Wagner fineness appear to be as-

TABLE 4–3. *Frequency distribution of cements with respect to expansion of prisms in the potential-sulfate-expansion test*

Type cement	0 to 0.020	0.020 to 0.040	0.040 to 0.060	0.060 to 0.080	0.080 to 0.100	0.100 to 0.120	0.120 to 0.140	0.140 to 0.160	0.160 to 0.180	0.180 to 0.200	0.200 to 0.250	0.250 to 0.300	0.300 to 0.350	0.350 to 0.400	0.400 and Over	Total
	Percentage expansion at 84 days — Number of cements															
I			1	6	7	4	8	8	4	4	10	7	7	1	8	75
IA				1	1		1		2		2				1	8
II*		5	5	1	4								1			16
IIA*				1												1
II		1	16	23	6	1	1									48
IIA					1											1
III		2	6	2	2	2	1	1				2				18
IIIA								1								1
IV, V		5	7	2	1											15
Total		13	35	36	22	7	11	10	6	4	12	9	8	1	9	183

*Classified as type I and IA when procured.

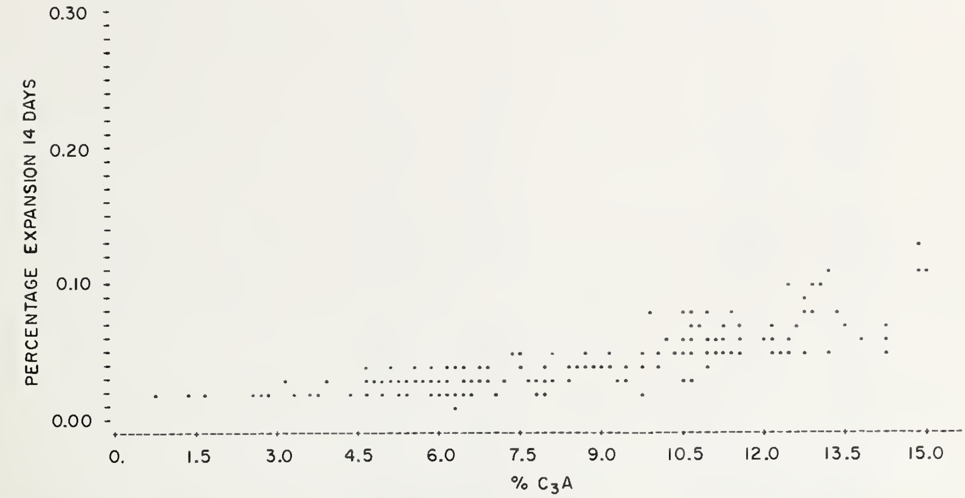


Figure 4–2. *Results of plotting the percentage expansion at 14 days versus the potential tricalcium aluminate content of the portland cements.*

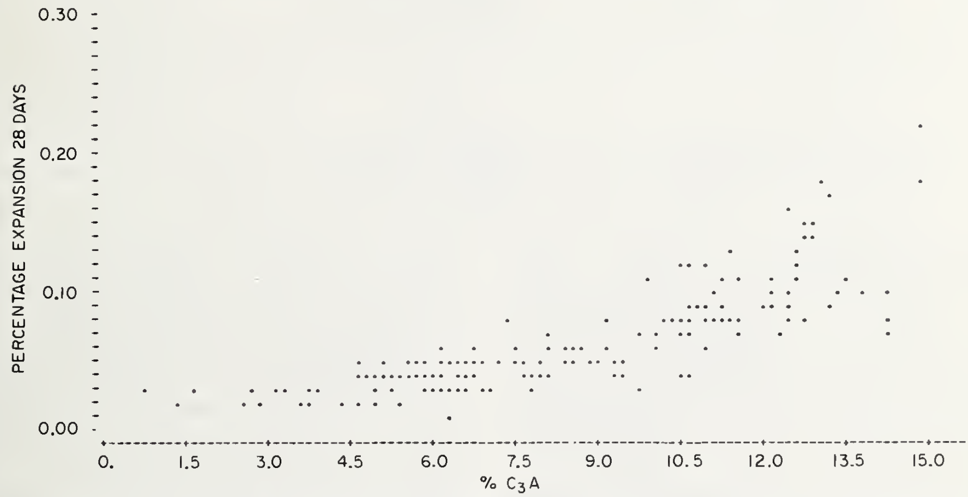


Figure 4–3. *Results of plotting the percentage expansion at 28 days versus the potential tricalcium aluminate content of the portland cements.*

sociated with cements having low expansion values. In general, the plots for an independent variable at the different ages were similar and the quadrant sum values [10] were about the same, irrespective of age.

The results of plotting all values of sulfate expansion for 14, 28, and 84 days versus C_3A content are shown in figures 4–2, 4–3, and 4–4, respectively. (These plots were made by the computer-printer and many of the dots represent more than one plotted point. Thus the concentration of values in some regions is not clearly indicated.) Certain cements, as will be indicated later, were not included in these plots. It may be noted that although there appears to be a fairly good relationship between the expansion values and the potential C_3A content, the band is rather broad in that a given expansion value is associated with cements having a considerable range in C_3A content, or with a given potential C_3A content a range of expansion values is obtained. It may also be noted that the relationship for cements of 0 to 9 percent C_3A appears to have a much lower slope than that for cements above the 7 to 9 percent C_3A range, especially at the later ages.

It was apparent in computing a variety of trial equations that some of the cements always had large deviations from the computed values. One of these cements had a high autoclave expansion (5.5 percent), with an MgO content of 1.4 percent. This cement also failed to meet the 28-day compressive strength requirement. Another cement had a 24-hour compressive strength of only 120 psi and also failed to meet the 3- and 28-day strength

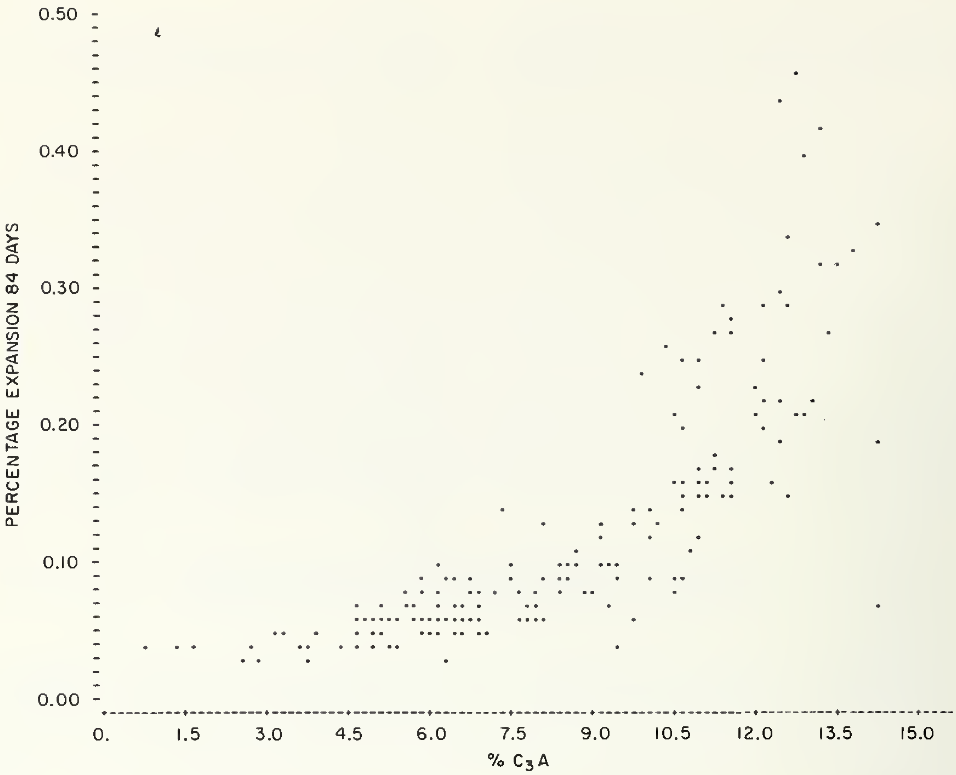


FIGURE 4–4. *Results of plotting the percentage expansion at 84 days versus the potential tricalcium aluminate content of the portland cements.*

requirements. A third cement also had a larger expansion than would be expected for its C_3A content. This cement had a high Zr content, of the order of 0.5 percent, and a relatively low 1-day compressive strength. Although these cements as well as the three white portland cements were used in preliminary computations and in the graphs of figure 4–1, they were not used in the final equations presented in this section nor in figures 4–2, 4–3, and 4–4. The white portland cements were not included because of the low Fe_2O_3 content as compared to other portland cements. Preliminary plots indicated that the expansion values of the white portland cements were higher than for other cements of comparable potential C_3A content. This confirms a previous report [13] which indicated that the reactions involved with white portland cement are different from those of other cements.

6.2. Expansion of Low C_3A Cements at 14 Days

In table 4–4 (p. 7) are presented coefficients for equations relating the 14-day expansion of the prisms of the cements having 0 to 9 percent C_3A to various independent variables. The S.D. values with C_3A or Al_2O_3 as the sole independent variables obtained for equations 1 and 2 for AE+NAE cements and equations 8 and 9 for the NAE cements were significantly lower than the S.D.'s for the expansion values of groups of cements as indicated in the footnotes 1 and 2 of this table. (In this and other instances where a relationship is said to be significantly improved in the second of two equations by the inclusion of one or more additional variables, refer to table 4–20 where ratios of variances for the reduction in error variance are given. See also the discussion in part 1 of this series.) Chemical limitations of C_3A, C_3S, Al_2O_3, C_4AF, Fe_2O_3, and SiO_2 have all been employed in specification requirements for sulfate-resisting cements. Equations 3 and 10 using these variables have lower S.D. values than when C_3A or Al_2O_3 are used as the only independent variable. However, the coefficient/s.d. ratios of three of the five in-

TABLE 4–5. *Calculated contributions of independent variables to 14-day sulfate expansion of cements having 0 to 8 percent* C_3A

Independent variable	Values used for independent variable	Coefficients from equation 12, table 4–4	Calculated contribution to SE_{14}	Calculated range of contribution to SE_{14}
			Const.=+0.042	
C_3A	0–8	+0.004	+0 to +0.032	0.032
Fe_2O_3	0–5.5	+0.007	+0 to +0.038	0.038
CaO/SiO$_2$	2.4–3.3	−0.025	−0.60 to −0.082	0.022
Insol	0–1.0	−0.013	+0 to −0.013	0.013
Loss	0–3.0	+0.003	0 to +0.009	0.009
K_2O	0–1.0	+0.010	0 to +0.010	0.010
SrO	0–0.4	+0.012	0 to +0.005	0.005
Cu	0–0.05	−0.150	0 to −0.007	0.007
V	0–0.1	+0.054	0 to +0.005	0.005
Zn	0–0.2	+0.021	0 to +0.004	0.004

TABLE 4–4. *Coefficients for equations relating the 14-day sulfate expansion of cements with 0 to 9 percent C_3A to various independent variables*

Equation	Type cement	Note	Const.	C_3A	Al_2O_3	C_3S	Fe_2O_3	SiO_2	$\frac{CaO}{SiO_2}$	$\frac{S}{A+F}$	Insol.	Loss	K_2O	SrO	Cu	V	Zn	S.D.
1	AE+NAE	(1)	SE_{14}=+0.0141 s.d.= (0.0022)	+0.0026 (0.0003)														0.00646
2	do	(1)	SE_{14}=−0.0073 s.d.= (0.0036)		+0.0082 (0.0008)													0.00565
3	do	(1)	SE_{14}=+0.0489 s.d.= (0.0353)	*−0.0077 (0.0188)	*+0.0028 (0.0499)	−0.00042 (0.00013)	*−0.0152 (0.0318)	−0.0012 (0.0010)										0.00537
4	do	(1)	SE_{14}=+0.0501 s.d.= (0.0124)	+0.0044 (0.0004)			+0.0064 (0.0008)		−0.0269 (0.0056)		−0.0121 (0.0042)	+0.0030 (0.0010)	+0.0112 (0.0028)					0.00489
5	do	(1)	SE_{14}=+0.0446 s.d.= (0.0122)	+0.0045 (0.0004)			+0.0069 (0.0009)		−0.0260 (0.0054)		−0.0135 (0.0041)	+0.0032 (0.0009)	+0.0105 (0.0028)	+0.0126 (0.0082)	−0.1471 (0.0600)	+0.0537 (0.0243)	+0.0203 (0.0156)	0.00464
6	do	(1)	SE_{14}=+0.0323 s.d.= (0.0166)		+0.0124 (0.0015)				−0.0252 (0.0056)	+0.0020 (0.0017)	−0.0119 (0.0043)	+0.0031 (0.0010)	+0.0114 (0.0028)					0.00491
7	do	(1)	SE_{14}=+0.0301 s.d.= (0.0164)		+0.0126 (0.0015)				−0.0247 (0.0053)	+.0017 (0.0017)	−0.0135 (0.0041)	+0.0032 (0.0009)	+0.0105 (0.0028)	+0.0128 (0.0082)	−0.1586 (0.0579)	+0.0520 (0.0241)	+0.0217 (0.0156)	0.00464
8	NAE	(2)	SE_{14}=+0.0149 s.d.= (0.0022)	+0.0024 (0.0003)														0.00642
9	do	(2)	SE_{14}=−0.0061 s.d.= (0.0036)		+0.0079 (0.0008)													0.00549
10	do	(2)	SE_{14}=+0.0452 s.d.= (0.0352)	*−0.0083 (0.0187)	*+0.0295 (0.0495)	−0.00039 (0.00013)	*−0.0158 (0.0316)	−0.0011 (0.0010)										0.00526
11	do	(2)	SE_{14}=+0.0476 s.d.= (0.0125)	+0.0042 (0.0004)			+0.0065 (0.0008)		−0.0258 (0.0056)		−0.0107 (0.0043)	+0.0032 (0.0010)	+0.0103 (0.0082)					0.00480
12	do	(2)	SE_{14}=+0.0418 s.d.= (0.0122)	+0.0043 (0.0004)			+0.0071 (0.0008)		−0.0249 (0.0053)		−0.0126 (0.0042)	+0.0033 (0.0009)	+0.0095 (0.0029)	+0.0116 (0.0081)	−0.1503 (0.0588)	+0.0545 (0.0238)	+0.0217 (0.0153)	0.00453
13	do	(2)	SE_{14}=+0.0307 s.d.= (0.0164)		+0.0121 (0.0015)				−0.0245 (0.0055)	+0.0022 (0.0017)	−0.0105 (0.0043)	+0.0032 (0.0009)	+0.0107 (0.0028)					0.00477
14	do	(2)	SE_{14}=+0.0281 s.d.= (0.0163)		+0.0124 (0.0014)				−0.0239 (0.0053)	+0.0019 (0.0017)	−0.0124 (0.0042)	+0.0033 (0.0009)	+0.0098 (0.0029)	+0.0118 (0.0081)	−0.1479 (0.0565)	+0.0554 (0.0236)	+0.0224 (0.0152)	0.00451

[1] 104 cements, avg=0.0306, S.D.=0.00812. [2] 99 cements, avg=0.0301, S.D.=0.00787. *Coefficient/s.d. less than 1.

TABLE 4–6. *Coefficients for equations relating the 28-day sulfate expansion of cements with 0 to 9 percent* C_3A *to various independent variables*

Equation	Type cement	Note	Const.	C_3A	$(C_3A)^2$	C_3S	Al_2O_3	$(Al_2O_3)^2$	Fe_2O_3	SiO_2	$\frac{CaO}{SiO_2}$	Insol	Loss	K_2O	SrO	Cu	Ni	S.D.
1	AE+NAE	(1)	SE_{28}=+0.0154 s.d.= (0.0031)	+0.0041 (0.0005)	------	------	------	------	------	------	------	------	------	------	------	------	------	0.00912
2	do	(1)	SE_{28}=−0.0146 s.d.= (0.0054)	------	------	------	+0.0122 (0.0012)	------	------	------	------	------	------	------	------	------	------	0.00833
3	do	(1)	SE_{28}=+0.1130 s.d.= (0.0511)	*−0.0041 (0.0273)	------	−0.00069 (0.00019)	*+0.0210 (0.0723)	------	*−0.0116 (0.0461)	−0.0031 (0.0015)	------	------	------	------	------	------	------	0.00833
4	do	(1)	SE_{28}=+0.0611 s.d.= (0.0188)	+0.0064 (0.0006)	------	------	------	------	+0.0082 (0.0013)	------	−0.0344 (0.0084)	−0.0161 (0.0064)	+0.0045 (0.0015)	+0.0139 (0.0042)	------	------	------	0.00738
5	do	(1)	SE_{28}=+0.0741 s.d.= (0.0188)	------	+0.00054 (0.00005)	------	------	------	+0.0088 (0.0012)	------	−0.0340 (0.0081)	−0.0175 (0.0062)	+0.0046 (0.0014)	+0.0149 (0.0041)	------	------	------	0.00719
6	do	(1)	SE_{28}=+0.0572 s.d.= (0.0181)	+0.0063 (0.0006)	------	------	------	------	+0.0084 (0.0013)	------	−0.0338 (0.0081)	−0.0165 (0.0062)	+0.0043 (0.0014)	+0.0124 (0.0043)	+0.0186 (0.0124)	−0.1284 (0.0733)	+0.5387 (0.2142)	0.00704
7	do	(1)	SE_{28}=+0.0692 s.d.= (0.0183)	------	+0.00054 (0.00005)	------	------	------	+0.0090 (0.0013)	------	−0.0327 (0.0078)	−0.0181 (0.0061)	+0.0044 (0.0014)	+0.0131 (0.0042)	+0.0130 (0.0123)	−0.1314 (0.0722)	+0.4963 (0.2104)	0.00692
8	do	(2)	odd SE_{28}=+0.0790 s.d.= (0.0238)	------	+0.00060 (0.00007)	------	------	------	+0.0101 (0.0018)	------	−0.0397 (0.0104)	−0.0192 (0.0103)	+0.0050 (0.0017)	+0.0139 (0.0059)	+0.0369 (0.0174)	−0.1701 (0.0967)	+0.5495 (0.3416)	0.00628
9	do	(2)	even SE_{28}=+0.0669 s.d.= (0.0326)	------	+0.00048 (0.00007)	------	------	------	+0.0078 (0.0021)	------	−0.0283 (0.0136)	−0.0145 (0.0090)	+0.0027 (0.0026)	+0.0138 (0.0064)	*−0.0133 (0.0193)	−0.1226 (0.1167)	+0.5475 (0.3105)	0.00763
10	do	(1)	SE_{28}=+0.0603 s.d.= (0.0188)	------	------	------	+0.0169 (0.0016)	------	−0.0026 (0.0011)	------	−0.0343 (0.0084)	−0.0158 (0.0064)	+0.0044 (0.0015)	+0.0137 (0.0042)	------	------	------	0.00740
11	do	(1)	SE_{28}=+0.0989 s.d.= (0.0206)	------	------	------	------	+0.0020 (0.0002)	−0.0029 (0.0011)	------	−0.0349 (0.0083)	−0.0152 (0.0063)	+0.0042 (0.0014)	+0.0140 (0.0041)	------	------	------	0.00727
12	do	(1)	SE_{28}=+0.0564 s.d.= (0.0181)	------	------	------	+0.0168 (0.0016)	------	−0.0023 (0.0011)	------	−0.0335 (0.0081)	−0.0163 (0.0062)	+0.0043 (0.0014)	+0.0122 (0.0043)	+0.0185 (0.0124)	−0.1313 (0.0745)	+0.5343 (0.2146)	0.00705
13	do	(1)	SE_{28}=+0.0953 s.d.= (0.0198)	------	------	------	------	+0.0019 (0.0002)	−0.0025 (0.0011)	------	−0.0343 (0.0074)	−0.0159 (0.0061)	+0.0040 (0.0014)	+0.0119 (0.0042)	+0.0169 (0.0122)	−0.1558 (0.0725)	+0.4766 (0.2106)	0.00693

[1] 104 cements. avg=0.0415, S.D.=0.0120. [2] 52 cements. *Coefficient/s.d. less than 1.

TABLE 4-6. *Coefficients for equations relating the 28-day sulfate expansion of cements with 0 to 9 percent* C_3A *to various independent variables*—Continued

Equation	Type cement	Note	Const.	C_3A	$(C_3A)^2$	C_3S	Al_2O_3	$(Al_2O_3)^2$	Fe_2O_3	SiO_2	$\frac{CaO}{SiO_2}$	Insol	Loss	K_2O	SrO	Cu	Ni	S.D.
14	NAE	[1]	SE_{26}=+0.0167 s.d.= (0.0031)	+0.0039 (0.0005)														0.00903
15	do	[1]	SE_{28}=−0.0125 s.d.= (0.0052)				+0.0116 (0.0011)											0.00805
16	do	[1]	SE_{28}=+0.1061 s.d.= (0.0511)	*−0.0039 (0.0271)		−0.00066 (0.00019)	*+0.0202 (0.0719)		*−0.0107 (0.0459)	−0.0029 (0.0015)								0.00763
17	do	[1]	SE_{28}=+0.0585 s.d.= (0.0188)	+0.0061 (0.0006)					+0.0085 (0.0013)		−0.0333 (0.0084)	−0.0144 (0.0065)	+0.0047 (0.0014)	+0.0119 (0.0043)				0.00725
18	do	[1]	SE_{28}=+0.0702 s.d.= (0.0192)		+0.00052 (0.00005)				+0.0090 (0.0013)		−0.0325 (0.0082)	−0.0157 (0.0065)	+0.0048 (0.0014)	+0.0136 (0.0042)				0.00717
19	do	[1]	SE_{28}=+0.0554 s.d.= (0.0181)	+0.0061 (0.0006)					+0.0087 (0.0013)		−0.0329 (0.0081)	−0.0153 (0.0063)	+0.0046 (0.0014)	+0.0101 (0.0043)	+0.0189 (0.0123)	−0.1290 (0.0722)	+0.5091 (0.2121)	0.00691
20	do	[1]	SE_{28}=+0.0661 s.d.= (0.0187)		+0.00051 (0.00005)				+0.0092 (0.0013)		−0.0315 (0.0080)	−0.0168 (0.0063)	+0.0045 (0.0014)	+0.0116 (0.0043)	+0.0139 (0.0124)	−0.1294 (0.0721)	+0.4725 (0.2116)	0.00691
21	do	[2]	SE^{odd}_{28}=+0.0529 s.d.= (0.0277)		+0.00050 (0.00008)				+0.0099 (0.0020)		−0.0293 (0.0115)	−0.0296 (0.0127)	+0.0084 (0.0023)	+0.0194 (0.0070)	+0.0358 (0.0182)	−0.1594 (0.1076)	*−0.0673 (0.3896)	0.00719
22	do	[2]	SE^{even}_{28}=+0.0672 s.d.= (0.0244)		+0.00056 (0.00007)				+0.0096 (0.0017)		−0.0321 (0.0105)	−0.0175 (0.0074)	+0.0022 (0.0018)	+0.0110 (0.0055)	*−0.0124 (0.0165)	*−0.0808 (0.0978)	+0.9087 (0.2615)	0.00616
23	do	[1]	SE_{28}=+0.0578 s.d.= (0.0188)				+0.0162 (0.0017)		−0.0019 (0.0011)		−0.0330 (0.0084)	−0.0141 (0.0065)	+0.0047 (0.0014)	+0.0118 (0.0043)				0.00726
24	do	[1]	SE_{28}=+0.0941 s.d.= (0.0208)					+0.0019 (0.0002)	−0.0022 (0.0011)		−0.0335 (0.0083)	−0.0135 (0.0064)	+0.0044 (0.0014)	+0.0124 (0.0042)				0.00718
25	do	[1]	SE_{28}=+0.0548 s.d.= (0.0181)				+0.0161 (0.0016)		−0.0016 (0.0011)		−0.0327 (0.0081)	−0.0151 (0.0063)	+0.0046 (0.0014)	+0.0099 (0.0043)	+0.0188 (0.0123)	−0.1318 (0.0723)	+0.5040 (0.2124)	0.00692
26	do	[1]	SE_{28}=+0.0914 s.d.= (0.0200)					+0.0019 (0.0002)	−0.0018 (0.0011)		−0.0332 (0.0080)	−0.0148 (0.0062)	+0.0043 (0.0014)	+0.0101 (0.0043)	+0.0175 (0.0122)	−0.1537 (0.0717)	+0.4513 (0.2096)	0.00685

99 cements; avg.=0.0407; S.D.=0.0116. [2] 49 cements. *Coefficient/s.d. less than 1.

dependent variables used in these equations were less than one. The potential C_4AF values were not used as they are computed as a constant times the Fe_2O_3 values. These equations also are affected by the interaction of C_3A, Al_2O_3, and Fe_2O_3, since the Al_2O_3 and Fe_2O_3 values are both used in calculating the potential C_3A values.

Using commonly determined independent variables as indicated in equations 4 and 6 as well as in equations 11 and 13 resulted in large reductions in the S.D. values as compared with those obtained in equations 1 and 2 or in 8 and 9, respectively. The use of additional minor constituents or trace elements indicated in equations 5, 7, 12, and 14 also resulted in further significant reductions in the S.D. as compared with equations 4, 6, 11, and 13, respectively. Various other independent variables were used in equations but none of them resulted in a better fit to the computed relationship.

Using values of 0 to 8 percent C_3A and approximate ranges of the other independent variables as presented in part 1, sections 1, 2, and 3 [10, 11, 12] and the coefficients from equation 12 of table 4–4, the calculated contributions to the percentage expansion of the prisms are presented in table 4–5. A value of 8 percent C_3A was used in this table as well as in tables 4–7 and 4–9 inasmuch as it is the upper specification limit for moderate sulfate resisting cement. For cements not considered sulfate resisting, a value of 8 percent was used as the lower limit as in tables 4–11, 4–13, and 4–15. Also presented in this table are the calculated ranges of the computed values. Some of the limitations of such computations and values have previously been discussed (10).

6.3. Expansion of Low C_3A Cements at 28 Days

In table 4–6 are presented coefficients for equations relating the 28-day expansion of the mortar prisms of cements having 0 to 9 percent C_3A to various independent variables. Again it may be noted that with the use of C_3A or Al_2O_3 as the sole independent variables, the S.D. values for equations 1 and 2 or 14 and 15 were significantly smaller than the overall S.D. for expansion values alone (see footnotes in table 4–6). Equations 3 and 16 illustrate the results obtained when commonly specified variables are employed as independent variables. When other commonly determined independent variables were used as in equations 4 and 10 for the AE+NAE cements or equations 17 and 23 for the NAE cements, the S.D. values were significantly lower. When minor or trace elements were included with the commonly determined independent variables as indicated in equations 6 and 12 or 19 and 25, the S.D. values were again reduced significantly. It may be noted that V and Zn had coefficient/s.d. ratios greater than one in the equations for the 14-day-expansion values (table 4–4). With 28-day expansion, however, these two variables were not significant and were replaced by Ni in the 28-day expansion equations. Equations 8 and 9 as well as 21 and 22 (table 4–6) illustrate the effect on the coefficients and s.d. values when using only the "odd" or "even" cements in the array as compared to the coefficients and s.d. values obtained when using all the cements as in equations 7 and 20, respectively. The extent of agreement of the values computed for the two groups of cements indicated to some extent the confidence which could be placed in the coefficients of the different variables in the equation. When $(C_3A)^2$ was used instead of C_3A or $(Al_2O_3)^2$ instead of Al_2O_3, the S.D. values obtained were lower in every instance. The use of other independent variables did not cause any appreciable reduction in the S.D. values.

Using values of 0 to 8 percent C_3A and approximate ranges of the other independent variables as previously determined together with the coefficients from equation 19 of table 4–6, the calculated contributions to the percentage 28-day expansion of the prisms are presented in table 4–7. Also presented in this table are the calculated ranges of the computed values for the various independent variables.

TABLE 4–7. *Calculated contributions of independent variables to 28-day sulfate expansion of cements having 0 to 8 percent* C_3A

Independent variable	Values used for independent variables	Coefficients from equation 19, table 4–6	Calculated contribution to SE_{28}	Calculated range of contribution to SE_{28}
			Const.=+0.055	
C_3A	0 –8	+0.0061	0 to +0.049	0.049
Fe_2O_3	0 –5.5	+0.0087	0 to +0.048	0.048
CaO/SiO_2	2.4–3.3	–0.0329	–0.079 to –0.109	0.030
Insol	0 –1.0	–0.0153	0 to –0.015	0.015
Loss	0 –3.0	+0.0046	0 to +0.014	0.014
K_2O	0 –1.0	+0.010	0 to +0.010	0.010
SrO	0 –0.4	+0.019	0 to +0.008	0.008
Cu	0 –0.05	–0.13	0 to –0.006	0.006
Ni	0 –0.02	+0.51	0 to +0.010	0.010

6.4. Expansion of Low C_3A Cements at 84 Days

In table 4–8 are presented coefficients for equations relating the 84-day expansion of the prisms of the cements having 0 to 9 percent C_3A to various independent variables. As in the equations developed for the 14- and 28-day expansion, the use of certain commonly determined independent variables resulted in a large decrease in the S.D. values, and with the use of certain minor or trace elements, a further significant decrease in the S.D. values was attained. Also, as in equations developed for the 28-day expansion, the use of $(C_3A)^2$ resulted in slightly lower S.D. values than was obtained when C_3A was used.

Presented in table 4–9 are calculated contributions of the various independent variables to the percentage expansion at 84 days together with the calculated ranges of the computed values. These values were computed on the basis of the coeffi-

TABLE 4–8. *Coefficients for equations relating the 84-day sulfate expansion of cements with 0 to 9 percent C_3A to various independent variables*

Equation	Type cement	Note	Const.	C_3A	$(C_3A)^2$	Al_2O_3	$(Al_2O_3)^2$	C_3S	SiO_2	Fe_2O_3	$\frac{CaO}{SiO_2}$	Insol.	Loss	K_2O	SrO	Cu	Ni	S.D.
1	AE+NAE	[1]	SE_{84}=+0.0141 s.d.= (0.0054)	+0.0084 (0.0008)														0.0158
2	do	[1]	SE_{84}=+0.0366 s.d.= (0.0033)		+0.00071 (0.00007)													0.0157
3	do	[1]	SE_{84}=−0.0364 s.d.= (0.0102)			+0.0226 (0.0022)												0.0158
4	do	[1]	SE_{84}=+0.0495 s.d.= (0.0111)	+0.0093 (0.0008)				−0.00084 (0.00023)										0.0150
5	do	[1]	SE_{84}=+0.1848 s.d.= (0.0936)	+0.0077 (0.0015)				−0.00114 (0.00034)	−0.0051 (0.0028)	*+0.0011 (0.0036)								0.0142
6	do	[1]	SE_{84}=+0.0829 s.d.= (0.0354)	+0.0117 (0.0012)						+0.0111 (0.0024)	−0.0493 (0.0159)	−0.0286 (0.0120)	+0.0046 (0.0028)	+0.0242 (0.0079)				0.0139
7	do	[1]	SE_{84}=+0.1086 s.d.= (0.0352)		+0.00100 (0.00009)					+0.0124 (0.0023)	−0.0494 (0.0151)	−0.0313 (0.0117)	+0.0049 (0.0027)	+0.0259 (0.0076)				0.0134
8	do	[1]	SE_{84}=+0.0740 s.d.= (0.0334)	+0.0114 (0.0011)						+0.0109 (0.0024)	−0.0476 (0.0149)	−0.0284 (0.0114)	+0.0044 (0.0027)	+0.0226 (0.0079)	+0.0451 (0.0229)	−0.1944 (0.1356)	+1.191 (0.396)	0.0130
9	do	[1]	SE_{84}=+0.0972 s.d.= (0.0336)		+0.00098 (0.00009)					+0.0123 (0.0024)	−0.0465 (0.0144)	−0.0314 (0.0112)	+0.0045 (0.0026)	+0.0238 (0.0077)	+0.0346 (0.0225)	−0.2004 (0.1324)	+1.116 (0.386)	0.0127
10	do	[1]	SE_{84}=+0.1519 s.d.= (0.0388)				+0.0036 (0.0003)			−0.0092 (0.0020)	−0.0500 (0.0156)	−0.0269 (0.0118)	+0.0041 (0.0027)	+0.0244 (0.0078)				0.0137
11	do	[1]	SE_{84}=+0.1422 s.d.= (0.0367)				+0.0035 (0.0003)			−0.0087 (0.0020)	−0.0483 (0.0148)	−0.0273 (0.0113)	+0.0039 (0.0026)	+0.0218 (0.0078)	+0.0422 (0.0227)	−0.2434 (0.1347)	+1.078 (0.391)	0.0129
12	NAE	[2]	SE_{84}=+0.0164 s.d.= (0.0054)	+0.0080 (0.0008)														0.0155
13	do	[2]	SE_{84}=+0.0378 s.d.= (0.0034)		+0.00067 (0.00007)													0.0156
14	do	[2]	SE_{84}=−0.0324 2.d.= (0.0099)			+0.0214 (0.0021)												0.0151
15	do	[2]	SE_{84}=+0.0511 s.d.= (0.0110)	+0.0089 (0.0008)				−0.00083 (0.00023)										0.0147
16	do	[2]	SE_{84}=+0.1766 s.d.= (0.0932)	+0.0073 (0.0015)				−0.00108 (0.00034)	−0.0049 (0.0028)	*+0.0016 (0.0036)								0.0139
17	do	[2]	SE_{84}=+0.0779 s.d.= (0.0356)	+0.0111 (0.0017)						+0.0114 (0.0024)	−0.0468 (0.0159)	−0.0253 (0.0123)	+0.0051 (0.0027)	+0.0208 (0.0081)				0.0137
18	do	[2]	SE_{84}=+0.1013 s.d.= (0.0360)		+0.00095 (0.00010)					+0.0124 (0.0024)	−0.0464 (0.0154)	−0.0280 (0.0121)	+0.0052 (0.0027)	+0.0237 (0.0079)				0.0134
19	do	[2]	SE_{84}=+0.0706 s.d.= (0.0336)	+0.0110 (0.0011)						+0.0114 (0.0024)	−0.0458 (0.0150)	−0.0265 (0.0117)	+0.0049 (0.0026)	+0.0186 (0.0081)	+0.0448 (0.0228)	−0.1968 (0.1341)	+1.131 (0.394)	0.0128
20	do	[2]	SE_{84}=+0.0915 s.d.= (0.0344)		+0.00093 (0.00010)					+0.0124 (0.0024)	−0.0441 (0.0147)	−0.0292 (0.0116)	+0.0049 (0.0026)	+0.0212 (0.0080)	+0.2353 (0.0229)	−0.1983 (0.1329)	+1.067 (0.390)	0.0127
21	do	[2]	SE_{84}=+0.1425 s.d.= (0.0393)				+0.0034 (0.0004)			−0.0079 (0.0021)	−0.0471 (0.0157)	−0.0238 (0.0122)	+0.0045 (0.0027)	+0.0216 (0.0080)				0.0136
22	do	[2]	SE_{84}=+0.1348 s.d.= (0.0373)				+0.0033 (0.0003)			−0.0075 (0.0021)	−0.0460 (0.0149)	−0.0253 (0.0116)	+0.0043 (0.0026)	+0.0185 (0.0080)	+0.0423 (0.0228)	+0.2410 (0.1340)	+1.025 (0.391)	0.0128

[1] 104 cements; avg=0.062; S.D.=0.0225. [2] 99 cements; avg=0.0657; S.D.=0.0215. *Coefficient/s.d. less than 1.

TABLE 4–9. *Calculated contributions of independent variables to 84-day sulfate expansion of cements having 0 to 8 percent* C_3A

Independent variable	Values used for independent variable	Coefficients from equation 19, table 4–8	Calculated contribution to SE_{84}	Calculated range of contribution to SE_{84}
			Const. = +0.071	
C_3A	0 –8	+0.011	0 to +0.088	0.088
Fe_2O_3	0 –5.5	+0.011	0 to +0.061	0.061
CaO/SiO_2	2.4–3.3	−0.046	−0.101 to −0.152	0.051
Insol	0 –1.0	−0.026	0 to −0.026	0.026
Loss	0 –3.0	+0.005	0 to +0.015	0.015
K_2O	0 –1.0	+0.019	0 to +0.019	0.019
SrO	0 –0.4	+0.045	0 to +0.018	0.018
Cu	0 –0.05	−0.197	0 to −0.010	0.010
Ni	0 –0.02	+1.131	0 to +0.023	0.023

cients obtained in equation 19 of table 4–8 together with the ranges of the independent variables as previously determined.

6.5. Expansion of High C_3A Cements at 14 Days

In table 4–10 (p. 13) are presented coefficients for equations relating the 14-day expansion of prisms made of cements with 7 to 15 percent C_3A to various independent variables. Equations 1 through 6 were computed using the AE+NAE cements and equations 7 through 12 for the NAE cements only. Preliminary trial equations indicated that the second or third power of the C_3A values resulted in lower S.D. values than when the first power was used with the cements having 7 to 15 percent C_3A. Equations 1 and 7 indicate that the use of $(C_3A)^2$ by itself caused a large reduction in the S.D. values. As indicated by equations 2 and 8, an increase in C_3S was accompanied by a reduction in expansion of the prisms, and inclusion of this variable reduced the S.D. values significantly. When the other commonly determined variables were included as in equations 3 and 9, the S.D. values were further reduced significantly. The use of the minor constituents or trace elements, SrO, Cr, and V, as in equations 4 and 10 appeared to produce a further small reduction in the S.D. values. However, the coefficient/s.d. ratio for loss on ignition was reduced to less than one when these elements were included, and therefore loss was eliminated from the equation. Equations 5 and 6 as well as 11 and 12 using $(Al_2O_3)^2$ resulted in approximately the same S.D. values as were obtained using $(C_3A)^2$ for equations 3, 4, 9, and 10, respectively. The loss on ignition had a coefficient/s.d. ratio greater than one in the four equations using $(Al_2O_3)^2$ values. With the use of the trace elements, SrO, Cr, and V, S.D. values were not significantly reduced.

Using squared values of C_3A for the cements with 8 to 15 percent C_3A together with the approximate ranges of the other independent variables and with the coefficients of equation 10 of table 4–10, values were calculated for the contributions of the independent variables to the percentage expansion of the prisms. These values are presented in table 4–11 together with the calculated ranges of the computed values.

TABLE 4–11. *Calculated contributions of independent variables to 14-day sulfate expansion of cements having 8 to 15 percent* C_3A

Independent variable	Values used for independent variable	Coefficients from equation 10, table 4–10	Calculated contribution to SE_{14}	Calculated range of contribution to SE_{14}
			Const. = +0.1045	
$(C_3A)^2$	64–225	+0.00047	+0.030 to +0.106	0.076
Fe_2O_3	0–5.5	+0.0049	0 to +0.027	0.027
CaO/SiO_2	2.4–3.3	−0.0392	−0.094 to −0.130	0.036
SrO	0–0.4	−0.0392	0 to −0.016	0.016
Cr	0–0.02	+0.5263	0 to +0.011	0.011
V	0–0.1	−0.2491	0 to −0.025	0.025

6.6. Expansion of High C_3A Cements at 28 Days

In table 4–12 is presented a series of equations relating the 28-day expansion of the mortar prisms of cements having 7 to 15 percent C_3A to various independent variables. The use of $(C_3A)^2$ in equations 1 or 14 or $(Al_2O_3)^2$ in equations 10 or 23 resulted in a large reduction in the S.D. values. Comparing equations 2 with 3 or 15 with 16, it may be noted that the use of the potential C_3S content alone resulted in the same S.D. value as the use of a number of commonly determined independent variables. This was true for both the AE+NAE and the NAE cements. By including certain minor constituents or trace elements the S.D. values were further reduced to a significant degree as may be noted by comparing the S.D. values of equations 3 and 4, 11 and 12, 16 and 17, or 24 and 25.

The use of $(Al_2O_3)^2$ in equation 10 (for AE +NAE cements) and in equation 23 (for NAE cements) resulted in a higher S.D. than the use of $(C_3A)^2$ in corresponding equations 1 and 14. However, when Fe_2O_3, CaO/SiO_2, and three of the trace elements were included (equations 8 and 12 for AE+NAE cements and equations 21 and 25 for NAE cements) the S.D. was the same whether $(Al_2O_3)^2$ or $(C_3A)^2$ was used. The use of C_2S and S/(A+F) in place of C_3S alone (other variables remaining the same) produced the same S.D. as indicated in equations 7 and 9 or 20 and 22.

In trying many combinations of variables (for many of which trials the equations are not produced here) the suspicion arose that there was an interaction between some of the trace elements and calculated compounds or oxides. This means that the effect of one variable depends on the level of another variable which interacts with it. This is shown in table 4–12 by the results when the products $C_3A \times V$ and $Al_2O_3 \times V$ are included (equations 7, 9, and 13 for NAE+AE cements and 20, 22, and 26 for NAE cements). For $Al_2O_3 \times V$, for example (equations 12 and 13), S.D. is decreased significantly and the ratio coefficient/s.d. for the product term is appreciably greater than

Table 4–10. *Coefficients for equations relating the 14-day sulfate expansion of cements with 7 to 15 percent C_3A to various independent variables*

Equation	Type cement	Note	Const.	$(C_3A)^2$	$(Al_2O_3)^2$	C_3S	Fe_2O_3	$\frac{CaO}{SiO_2}$	Loss	SrO	Cr	V	S.D.
1	AE+NAE	(1)	SE_{14}=+0.0134 s.d.= (0.0033)	+0.00035 (0.00003)	----	----	----	----	----	----	----	----	0.0137
2	do	(1)	SE_{14}=+0.0419 s.d.= (0.0099)	+0.00035 (0.00003)	----	−0.00056 (0.00018)	----	----	----	----	----	----	0.0132
3	do	(1)	SE_{14}=+0.0994 s.d.= (0.0303)	+0.00044 (0.00004)	----	----	+0.0050 (0.0025)	−0.0396 (0.0119)	+0.0050 (0.0022)	----	----	----	0.0130
4	do	(1)	SE_{14}=+0.0974 s.d.= (0.0297)	+0.00046 (0.00004)	----	----	+0.0052 (0.0024)	−0.0373 (0.0115)	----	−0.0181 (0.0137)	+0.5751 (0.2830)	−0.2885 (0.1327)	0.0128
5	do	(1)	SE_{14}=+0.1302 s.d.= (0.0314)	----	+0.0022 (0.0002)	----	−0.0096 (0.0020)	−0.0440 (0.0121)	+0.0055 (0.0022)	----	----	----	0.0130
6	do	(1)	SE_{14}=+0.1340 s.d.= (0.0308)	----	+0.0023 (0.0002)	----	−0.0102 (0.0020)	−0.0454 (0.0118)	+0.0042 (0.0023)	*−0.0117 (0.0135)	+0.6154 (0.2805)	−0.2212 (0.1404)	0.0127
7	NAE	(2)	SE_{14}=+0.0138 s.d.= (0.0035)	+0.00034 (0.00003)	----	----	----	----	----	----	----	----	0.0139
8	do	(2)	SE_{14}=+0.0429 s.d.= (0.0104)	+0.00034 (0.00003)	----	−0.00057 (0.00019)	----	----	----	----	----	----	0.0134
9	do	(2)	SE_{14}=+0.1090 s.d.= (0.0322)	+0.00044 (0.00004)	----	----	+0.0045 (0.0026)	−0.0426 (0.0126)	+0.0053 (0.0023)	----	----	----	0.0132
10	do	(2)	SE_{14}=+0.1045 s.d.= (0.0314)	+0.00047 (0.00004)	----	----	+0.0049 (0.0025)	−0.0392 (0.0121)	----	−0.0392 (0.0143)	+0.5263 (0.2914)	−0.2491 (0.1377)	0.0129
11	do	(2)	SE_{14}=+0.1402 s.d.= (0.0335)	----	+0.0022 (0.0002)	----	−0.0101 (0.0022)	−0.0469 (0.0128)	+0.0056 (0.0023)	----	----	----	0.0131
12	do	(2)	SE_{14}=+0.1418 s.d.= (0.0327)	----	+0.0023 (0.0002)	----	−0.0107 (0.0021)	−0.0473 (0.0125)	+0.0041 (0.0025)	−0.0213 (0.0142)	+0.5549 (0.2900)	−0.1880 (0.1453)	0.0128

[1] 113 cements, avg=0.0521, S.D.=0.0216. [2] 102 cements, avg=0.0513, S.D.=0.0214. *Coefficient/s.d. less than 1.

TABLE 4–12. *Coefficients for equations relating the 28-day sulfate expansion of cements with 7 to 15 percent C_3A to various independent variables*

Equation	Type cement	Note	Const.	$(C_3A)^2$	$(Al_2O_3)^2$	C_3S	C_2S	Fe_2O_3	$\frac{CaO}{SiO_2}$	$\frac{S}{A+F}$	Insol.	MgO	Cr	V	P	$C_3A \times V$	$Al_2O_3 \times V$	S.D.
1	AE+NAE	[1]	SE_{28}=+0.0094 s.d.= (0.0056)	+0.00063 (0.00005)	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	0.0235
2	do	[1]	SE_{28}=+0.1112 s.d.= (0.0548)	+0.00071 (0.00007)	-----	-----	-----	+0.0060 (0.0044)	−0.0427 (0.0208)	-----	+0.0177 (0.0170)	−0.0027 (0.0020)	-----	-----	-----	-----	-----	0.0232
3	do	[1]	SE_{28}=+0.0404 s.d.= (0.0174)	+0.00062 (0.00005)	-----	−0.00061 (0.00032)	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	0.0232
4	do	[1]	SE_{28}=+0.0285 s.d.= (0.0157)	+0.00070 (0.00004)	-----	−0.00057 (0.00029)	-----	-----	-----	-----	-----	-----	+1.1832 (0.4455)	−0.4507 (0.2108)	−0.0749 (0.0159)	-----	-----	0.0205
5	do	[2]	SE_{28}^{odd}=+0.0343 s.d.= (0.0219)	+0.00066 (0.00006)	-----	−0.00050 (0.00040)	-----	-----	-----	-----	-----	-----	+0.8192 (0.5785)	−0.6173 (0.2729)	−0.0669 (0.0269)	-----	-----	0.0216
6	do	[2]	SE_{28}^{even}=+0.0217 s.d.= (0.0235)	+0.00074 (0.00006)	-----	−0.00067 (0.00043)	-----	-----	-----	-----	-----	-----	+1.8369 (0.7485)	*−0.2238 (0.3602)	−0.0786 (0.0200)	-----	-----	0.0199
7	do	[1]	SE_{28}=+0.0211 s.d.= (0.0159)	+0.00077 (0.00005)	-----	−0.00055 (0.00029)	-----	-----	-----	-----	-----	-----	+1.1056 (0.4411)	+1.7124 (1.1007)	−0.0692 (0.0160)	−0.2227 (0.1113)	-----	0.0202
8	do	[1]	SE_{28}=+0.0828 s.d.= (0.0478)	+0.00080 (0.00006)	-----	-----	-----	+0.0062 (0.0039)	−0.0376 (0.0185)	-----	-----	-----	+1.1068 (0.4453)	−0.4759 (0.2112)	−0.0761 (0.0160)	-----	-----	0.0205
9	do	[1]	SE_{28}=−0.0036 s.d.= (0.0176)	+0.00079 (0.00006)	-----	-----	+0.00066 (0.00030)	-----	-----	−0.0069 (0.0056)	-----	-----	+1.0837 (0.4383)	+1.6908 (1.0979)	−0.0689 (0.0159)	−0.2235 (0.1110)	-----	0.0202
10	do	[1]	SE_{28}=−0.0242 s.d.= (0.0098)	-----	+0.0031 (0.0003)	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	0.0265
11	do	[1]	SE_{28}=+0.1500 s.d.= (0.0561)	-----	+0.0035 (0.0003)	-----	-----	−0.0184 (0.0036)	−0.0459 (0.0212)	-----	-----	-----	-----	-----	-----	-----	-----	0.0234
12	do	[1]	SE_{28}=+0.1360 s.d.= (0.0502)	-----	+0.0039 (0.0003)	-----	-----	−0.0203 (0.0033)	−0.0438 (0.0190)	-----	-----	-----	+1.1415 (0.4504)	−0.5074 (0.2137)	−0.0735 (0.0161)	-----	-----	0.0207
13	do	[1]	SE_{28}=+0.1150 s.d.= (0.0497)	-----	+0.0043 (0.0003)	-----	-----	−0.0203 (0.0032)	−0.0412 (0.0186)	-----	-----	-----	+1.0280 (0.4422)	+4.3811 (1.9773)	−0.0659 (0.0160)	-----	−0.8670 (0.3487)	0.0202

[1] 113 cements, avg=0.0782, S.D.=0.0378. [2] 56 cements. *Coefficient/s.d. less than 1.

TABLE 4–12. *Coefficients for equations relating the 28-day sulfate expansion of cements with 7 to 15 percent* C_3A *to various independent variables*—Continued

Equation	Type cement	Note	Const.	$(C_3A)^2$	$(Al_2O_3)^2$	C_3S	C_2S	Fe_2O_3	$\frac{CaO}{SiO_2}$	$\frac{S}{A+F}$	Insol.	MgO	Cr	V	P	$C_3A \times V$	$Al_2O_3 \times V$	S.D.
14	NAE	(3)	SE_{28}=+0.0108 s.d.= (0.0060)	+0.00061 (0.00005)														0.0239
15	do	(3)	SE_{28}=+0.1186 s.d.= (0.0590)	+0.00069 (0.00007)				+0.0051 (0.0046)	−0.0437 (0.0223)		*+0.0176 (0.0202)	−0.0030 (0.0022)						0.0237
16	do	(3)	SE_{28}=+0.0418 s.d.= (0.0184)	+0.00060 (0.00005)		−0.00061 (0.00034)												0.0237
17	do	(3)	SE_{28}=+0.0302 s.d.= (0.0167)	+0.00069 (0.00005)		−0.00059 (0.00031)							+1.1676 (0.4712)	−0.4180 (0.2235)	−0.0725 (0.0165)			0.0210
18	do	(4)	SE_{28}^{odd}=+0.0191 s.d.= (0.0232)	+0.00068 (0.00007)		*−0.00022 (0.00042)							+0.6666 (0.6367)	−0.7583 (0.2768)	−0.0640 (0.0260)			0.0212
19	do	(4)	SE_{28}^{even}=+0.0436 s.d.= (0.0234)	+0.00070 (0.00006)		−0.00107 (0.00044)							+1.7599 (0.6823)	*+0.2748 (0.3708)	−0.0798 (0.0208)			0.0201
20	do	(3)	SE_{28}=+0.0227 s.d.= (0.0171)	+0.00076 (0.00006)		−0.00056 (0.00030)							+1.0651 (0.4699)	+1.6192 (1.1896)	−0.0680 (0.0165)	−0.2112 (0.1212)		0.0208
21	do	(3)	SE_{28}=+0.0922 s.d.= (0.0516)	+0.00079 (0.00007)				+0.0056 (0.0041)	−0.0400 (0.0198)				+1.1035 (0.4700)	−0.4409 (0.2239)	−0.0733 (0.0166)			0.0211
22	do	(3)	SE_{28}=−0.0070 s.d.= (0.0186)	+0.00076 (0.00007)			+0.00070 (0.00032)			−0.0058 (0.0058)			+1.0364 (0.4671)	+1.6210 (1.1869)	−0.0675 (0.0165)	−0.2141 (0.1208)		0.0208
23	do	(3)	SE_{28}=−0.0207 s.d.= (0.0105)		+0.0029 (0.0003)													0.0270
24	do	(3)	SE_{28}=+0.1614 s.d.= (0.0598)		+0.0034 (0.0004)			−0.0187 (0.0038)	−0.0485 (0.0226)									0.0239
25	do	(3)	SE_{28}=+0.1461 s.d.= (0.0541)		+0.0038 (0.0003)			−0.0204 (0.0034)	−0.0465 (0.0203)				+1.1358 (0.4741)	−0.4670 (0.2258)	−0.0704 (0.0167)			0.0212
26	do	(3)	SE_{28}=+0.1275 s.d.= (0.0537)		+0.0043 (0.0004)			−0.0206 (0.0033)	−0.0445 (0.0199)				+0.9980 (0.4691)	+4.1545 (2.1212)	−0.0640 (0.0166)		−0.8211 (0.3748)	0.0208

[3] 102 cements, avg=0.0769, S.D.=0.0373. [4] 51 cements. *Coefficient/s.d. less than 1.

TABLE 4–13. *Calculated contributions of independent variable to 28-day sulfate expansion of cements having 8 to 15 percent* C_3A

Independent variable	Values used for independent variable	Coefficients from equation 21, table 4–12	Calculated contribution to SE_{28}	Calculated range of contribution to SE_{28}
			Const.=+0.092	
$(C_3A)^2$	64 –225	+0.00079	+0.052 to +0.178	0.126
Fe_2O_3	0 – 5.5	+0.0056	0 to +0.031	0.031
CaO/SiO_2	2.4– 3.3	−0.04	−0.096 to −0.132	0.036
Cr	0 – 0.02	+1.1	0 to +0.022	0.022
V	0 – 0.1	−0.44	0 to −0.044	0.044
P	0 – 0.5	−0.07	0 to −0.035	0.035

2. Also, note that the coefficient for V changes from −0.5 (s.d. 0.2) to +4.3 (s.d. 2.0) while all the rest of coefficients and s.d.'s in the equation change very little. This indicates that there is a correlation between Al_2O_3 and V and that the effects of these two variables are not simply additive. The changes are significant also for the NAE cements (equations 25 and 26). There is some indication that the same situation holds for C_3A and V (equations 4 compared to 7 and 17 compared to 20), but the change in S.D. in this case was not large enough to be significant.

Using the squared values of 8 and 15 percent C_3A together with the approximate ranges of the other variables and the coefficients of equation 21 of table 4–12, the calculated values for the contributions to the percentage expansion of the prisms at 28 days are presented in table 4–13 together with the calculated ranges of the computed values.

6.7. Expansion of High C_3A Cements at 84 Days

In table 4–14 (p. 17) are presented coefficients for equations relating the 84-day expansion values of the prisms of the cements having 7 to 15 percent C_3A to various independent variables. The S.D. values using $(C_3A)^3$ or $(Al_2O_3)^3$ as independent variables as indicated in equations 1 and 8 for AE+NAE cements or 11 and 18 for the NAE cements were significantly lower than the S.D. values for the respective cements. The use in the equations of the CaO/SiO_2 ratio with the $(C_3A)^3$ or the CaO/SiO_2 ratio and Fe_2O_3 with the $(Al_2O_3)^3$ variable resulted in a significant reduction in the S.D. values as may be noted in equations 3 and 9 or in equations 13 and 19. The use of certain minor constituents as in equations 4 and 10 or in 14 and 20 resulted in further significant reduction in the S.D. values. The coefficients for the independent variables obtained when the "odds" and "evens" in the array of cements were computed separtely are presented in equations 5 and 6 for the AE+NAE cements and in equations 15 and 16 for the NAE cements.

Using the third power of the values of C_3A for cements with 8 to 15 percent C_3A together with the approximate ranges of the other independent variables and the coefficients from equation 14 of table 4–14, the calculated contributions to the percentage expansion at 84 days of the prisms are presented in table 4–15. Also presented in this table are the calculated ranges of the computed values.

TABLE 4–15. *Calculated contributions of independent variables to 84-day sulfate expansion of cements having 8 to 15 percent* C_3A

Independent variable	Values used for independent variable	Coefficients from equation 14, table 4–14	Calculated contribution to SE_{84}	Calculated range of contribution to SE_{84}
			Const.=+0.0330	
$(C_3A)^3$	512 –3375	+0.00017	+0.087 to +0.574	0.487
CaO/SiO_2	2.4– 3.3	−0.125	−0.300 to −0.413	0.113
Cr	0– 0.02	+3.37	0 to +0.066	0.066
V	0– 0.1	−0.78	0 to −0.078	0.078
P	0– 0.5	−0.25	0 to −0.125	0.125

TABLE 4–16. *Range and variance of duplicate tests as compared to the S.D. values obtained for equations at 14, 28, and 84 days*

Col. 1	Col. 2	Col. 3	Col. 4	Col. 5
Age of expansion measurement	Range of percentage expansion of 21 cements	$(\text{Variance})^{1/2}$ of duplicate tests	S.D. values of equations for NAE cements, table 4–17	Ratio of variances (squared values of column 4 divided by squared values of column 3)
Days	*Percent*			
14	0.014–0.056	0.0025	0.00443	3.2
28	0.016–0.083	0.0028	0.00649	5.3
84	0.025–0.185	0.0036	0.01168	10.6

6.8. Tests on a Supplementary Series of Cements

The 21 cements used in the supplementary tests to evaluate the reproducibility of the test method had expansion values within the range obtained for the type II, IV, and V cements in the studies reported in this article. The variance of duplicates calculated from these 21 cements was therefore compared to the $(S.D.)^2$ values obtained for the equations with the lowest S.D. values computed for the cements having 0 to 9 percent C_3A. The results of these comparisons are presented in table 4–16. The variances of the duplicate tests at each of the ages indicated were significantly lower than attained in the equations as judged by the ratio of variances as presented in the last column.

6.9. Autoclave Expansion and Sulfate Expansion

Information was not available on the glass content or rate of cooling of the clinker used in the manufacture of these cements. It has previously been reported that rapidly quenched clinker having high C_3A content has greater sulfate resistance than slowly cooled clinkers although this is not the case with the C_4AF constituent [2, 3]. It is also known that rapid quenching of high magnesia

TABLE 4–14. *Coefficients for equations relating the 84-day sulfate expansion of cements with 7 to 15 percent C_3A to various independent variables* [a]

Equation	Type cement	Note	Const.	$(C_3A)^3$	$(Al_2O_3)^3$	C_3S	Fe_2O_3	$\frac{CaO}{SiO_2}$	Cr	V	P	$C_3A \times V$	S.D.
1	AE+NAE	[1]	SE_{84}=+0.0019 s.d.= (0.0142)	+0.00014 (0.00001)									0.0803
2	do	[1]	SE_{84}=+0.0696 s.d.= (0.0588)	+0.00014 (0.00001)		−0.0013 (0.0011)							0.0802
3	do	[1]	SE_{84}=+0.4471 s.d.= (0.1810)	+0.00015 (0.00001)				−0.1464 (0.0637)					0.0789
4	do	[1]	SE_{84}=+0.3390 s.d.= (0.1651)	+0.00017 (0.00001)				−0.1292 (0.0581)	+3.5118 (1.541)	−0.7415 (0.7331)	−0.2549 (0.0559)		0.0713
5	do	[2]	$SE_{84}^{(odd)}$=+0.1694 s.d.= (0.1756)	+0.00016 (0.00001)				*−0.0595 (0.0615)	+2.3452 (1.5507)	−1.2776 (0.7351)	−0.2293 (0.0730)		0.0581
6	do	[1]	$SE_{84}^{(even)}$=+0.6486 s.d.= (0.3078)	+0.00020 (0.00002)				−0.2512 (0.1089)	+5.4264 (3.0919)	*−0.1693 (1.4984)	−0.2763 (0.0843)		0.0827
7	do	[1]	SE_{84}=+0.3267 s.d.= (0.1652)	+0.00018 (0.00001)				−0.1270 (0.0580)	+3.3374 (1.5458)	*+3.5797 (3.7692)	−0.2437 (0.0566)	−0.4436 (0.3796)	0.0711
8	do	[1]	SE_{84}=−0.0584 s.d.= (0.0255)		+0.00119 (0.00012)								0.0995
9	do	[1]	SE_{84}=+0.6002 s.d.= (0.2097)		+0.00135 (0.00013)		−0.0777 (0.0132)	−0.1576 (0.0767)					0.0853
10	do	[1]	SE_{84}=+0.5600 s.d.= (0.1965)		+0.00149 (0.00013)		−0.0842 (0.0125)	−0.1491 (0.0718)	+3.6312 (1.7242)	−0.9603 (0.8181)	−0.2290 (0.0621)		0.0794
11	NAE	[3]	SE_{84}=+0.0037 s.d.= (0.0153)	+0.00014 (0.00001)									0.0819
12	do	[3]	SE_{84}=+0.0599 s.d.= (0.0621)	+0.00014 (0.00001)		*−0.0010 (0.0012)							0.0820
13	do	[3]	SE_{84}=+0.4103 s.d.= (0.1943)	+0.00015 (0.00001)				−0.1435 (0.0684)					0.0805
14	do	[3]	SE_{84}=+0.3297 s.d.= (0.1767)	+0.00017 (0.00001)				−0.1250 (0.0622)	+3.3687 (1.6155)	−0.7767 (0.7711)	−0.2520 (0.0578)		0.0728
15	do	[4]	odd SE_{84}=+0.0992 s.d.= (0.1856)	+0.00015 (0.00001)				*−0.0348 (0.0645)	+2.3526 (1.6219)	−1.4287 (0.7520)	−0.2248 (0.0739)		0.0579
16	do	[4]	even SE_{84}=+0.7598 s.d.= (0.3234)	+0.00020 (0.00002)				−0.2881 (0.1153)	+5.2903 (3.1895)	*+0.2143 (1.5851)	−0.2766 (0.0867)		0.0846
17	do	[3]	SE_{84}=+0.3159 s.d.= (0.1766)	+0.00018 (0.00001)				−0.1230 (0.0620)	+3.0894 (1.6275)	+4.0735 (4.0390)	−0.2419 (0.0582)	−0.5014 (0.4099)	0.0726
18	do	[3]	SE_{84}=−0.0503 s.d.= (0.0273)		+0.00115 (0.00013)								0.1016
19	do	[3]	SE_{84}=+0.5769 s.d.= (0.2239)		+0.00129 (0.00014)		−0.0810 (0.0139)	−0.1422 (0.0815)					0.0868
20	do	[3]	SE_{84}=+0.5346 s.d.= (0.2099)		+0.00144 (0.00014)		−0.0868 (0.0131)	−0.1342 (0.0764)	+3.5563 (1.8026)	−0.9358 (0.8593)	−0.2202 (0.0641)		0.0811

[1] 113 cements, avg=0.1757, S.D.=0.1359. [2] 56 cements.
[3] 102 cements, avg=0.1746, S.D.=0.1350. [4] 51 cements. *Coefficient/s.d. less than 1.
[a] The discrepancy between the standard deviations for equations 5 and 6 and 15 and 16 in this case is due to the fact that both the estimated value and the one with the lowest negative deviation happened to fall in the group of evens. See part 1 of this series.

Table 4–17. *Coefficients for equations relating the sulfate expansion of cements having 0 to 9 percent C_3A to various independent variables*

Equation	Type cement	Note	Const.	C_3A	Fe_2O_3	$\frac{CaO}{SiO_2}$	Insol.	Loss	K_2O	SrO	Cu	V	Ni	Zn	(MgO× Auto.)	(C_3A× Auto.)	S.D.
1	AE+NAE	(1)	SE_{14}=+0.0489 s.d.= (0.0121)	+0.0040 (0.0005)	+0.0072 (0.0008)	−0.0265 (0.0053)	−0.0160 (0.0041)	+0.0033 (0.0009)	+0.0088 (0.0029)	*+0.0070 (0.0082)	−0.1708 (0.0587)	+0.0457 (0.0237)	------	+0.0210 (0.0153)	−0.0121 (0.0045)	+0.0080 (0.0028)	0.00449
2	do	(2)	SE_{28}=+0.0608 s.d.= (0.0173)	+0.0053 (0.0006)	+0.0090 (0.0012)	−0.0332 (0.0077)	−0.0212 (0.0059)	+0.0046 (0.0014)	+0.0063 (0.0042)	*+0.0083 (0.0121)	−0.1645 (0.0700)	------	+0.5680 (0.2016)	------	−0.0205 (0.0067)	+0.0149 (0.0041)	0.00660
3	do	(3)	SE_{84}=+0.0818 s.d.= (0.0312)	+0.0094 (0.0011)	+0.0123 (0.0022)	−0.0465 (0.0139)	−0.0381 (0.0108)	+0.0050 (0.0024)	+0.0143 (0.0076)	+0.0239 (0.0219)	−0.2697 (0.1269)	------	+1.2527 (0.3652)	------	−0.0426 (0.0121)	+0.0309 (0.0075)	0.01196
4	NAE	(4)	SE_{14}=+0.0459 s.d.= (0.0122)	+0.0038 (0.0005)	+0.0073 (0.0008)	−0.0252 (0.0053)	−0.0143 (0.0042)	+0.0034 (0.0009)	+0.0081 (0.0029)	*+0.0060 (0.0082)	−0.1699 (0.0579)	+0.0466 (0.0235)	------	+0.0229 (0.0152)	−0.0107 (0.0047)	+0.0077 (0.0031)	0.00443
5	do	(5)	SE_{28}=+0.0596 s.d.= (0.0173)	+0.0050 (0.0006)	+0.0090 (0.0012)	−0.0322 (0.0077)	−0.0184 (0.0060)	+0.0047 (0.0013)	+0.0069 (0.0042)	*+0.0073 (0.0121)	−0.1552 (0.0690)	------	+0.5115 (0.2004)	------	−0.0195 (0.0068)	+0.0156 (0.0045)	0.00649
6	do	(6)	SE_{84}=+0.0795 s.d.= (0.0312)	+0.0086 (0.0012)	+0.0122 (0.0022)	−0.0441 (0.0138)	−0.0330 (0.0108)	+0.0050 (0.0024)	+0.0114 (0.0075)	*+0.0195 (0.0218)	−0.2531 (0.1242)	------	+1.1342 (0.3607)	------	−0.0421 (0.0122)	+0.0340 (0.0080)	0.01168

[1] 104 cements, avg 0.0306, S.D.=0.00812. [2] 104 cements, avg 0.0415, S.D.=0.01201. [3] 104 cements, avg 0.0672, S.D.=0.02249. [4] 99 cements, avg 0.0298, S.D.=0.00787. [5] 99 cements, avg 0.0407, S.D.=0.01157. [6] 99 cements, avg 0.0657, S.D.=0.02153. *Coef./s.d. less than 1.

cements results in lower autoclave expansion. It is generally recognized then that the results of the autoclave expansion test are affected by (among other things) the rate of quenching of the cement clinker during manufacture. Attempts were therefore made to use this property to further reduce the S.D. values.

Equations were computed for both the cements containing 0 to 9 percent C_3A and those containing 7 to 15 percent C_3A including as an additional independent variable the autoclave expansion, ratios of autoclave expansion to MgO and/or C_3A contents, or the reciprocals of these values or the products of the MgO and/or C_3A values times the autoclave expansion values. The use of the products of the MgO and the C_3A times the autoclave expansion as additional independent variables in the equations resulted in significantly lower S.D. values only with the cements having 0 to 9 percent C_3A whereas this was not the case for cements having 7 to 15 percent C_3A. The equations 1, 4, 2, 5, 3, and 6 presented in table 4–17 for cements containing 0 to 9 percent C_3A may be compared with equations 5 and 12 of table 4–4, equations 6 and 19 of table 4–6, and equations 8 and 19 of table 4–8, respectively, in which other independent variables were the same. It may be noted in table 4–17 that SrO has a coefficient/s.d. ratio of less than 1 in five of the six equations, which was not the case in the previously reported comparable equations. It may also be noted that the sign of the coefficient for MgO× autoclave expansion was minus while that for the C_3A×autoclave expansion was plus. No satisfactory explanation can be offered for this apparent anomaly.

7. Discussion

In plotting the expansion values of the mortar prisms made of different cements versus the age of the measurement, it was noted that smooth lines could be drawn with only slight deviations of the plotted points from the lines. With cements having low expansion values, the rate of expansion at the later ages was not so great as at the earlier ages, i.e., 0 to 14 days or 14 to 28 days. Cements having high expansion values at the early ages had, in many instances, more rapid rates of expansion at the later ages. This occurred between 2 and 3 months with some cements. In some instances the specimens warped in the 4- to 6-month period, making the measurements after that condition had occurred of questionable value. Up to the age of 84 days the plots of expansion versus age indicated only few instances where the plotted lines of the different cements crossed one another. A greater difference between expansion values for different cements was obtained at 28 days than at 14 days, which could result in a better discrimination between the cements. The more rapid expansion after two months did not occur uniformly with all of the cements of high potential C_3A content.

Plotting the 14-, 28-, and 84-day sulfate expansion values of the different cements versus the various independent variables indicated that in general the same variables had a significant effect at the different ages.

The individual plots shown in figure 4–1 indicate no apparent relationship between the MgO contents of the cements and the expansion values. MgO also did not turn out to be a significant variable in equations relating the expansion at various ages to various independent variables. These expansion values were obtained at a relatively early age and it may be possible that the suspected effect of MgO is masked at the early ages and could become more apparent at the later ages. Some exploratory computations of the relationship of the expansion values at six months of the cements having 0 to 9 percent C_3A and the MgO content indicated no significant contribution of the MgO to the expansion. The MgO contents of the cements used in this study were all below 5.0 percent and it has previously been reported [2] that deleterious effects are obtained only with higher MgO contents.

It was noted in figure 4–1 that there was no apparent relationship between the potential C_3S content of the cement and the expansion of the mortar prisms of the different cements whereas there appeared to be some relationship to the potential C_2S content. In the computed equations there was evidence that high values of C_3S were associated with low expansion values or that Fe_2O_3 and the CaO/SiO_2 ratio were associated with the expansion values. The fact that high C_3S content of cements is usually associated with high early strength prompted calculations of equations relating the compressive strength of 2-inch motar cubes made from the cements to the sulfate expansion values obtained with the motar prisms.

Equations were computed for the relationship between the sulfate expansion values at 14, 28, and 84 days and the compressive strength at 1, 3, 7, and 28 days, and 1 year, of 2-inch mortar cubes made of 1 : 2.75 (cement to graded Ottawa sand) mortar stored in water after the original 24-hour moist curing. Also computed were equations with the strengths at the different ages and including $(C_3A)^2$ for the 14- and 28-day sulfate expansion and $(C_3A)^3$ for the 84-day expansion. These computations were all made without separating the cements into the two groups of high and low C_3A content. The equations for the AE+NAE and for the NAE cements are presented in table 4–18. The "F" values presented in the last column in this table show that when strength alone was used as the independent variable (equations 1 through 15 and 31 through 45) there was no relationship between the sulfate expansion and the compressive strength at 1, 3, 7, or 28 days but there was a significant relationship between the expansion at each of the 3 ages and the 1-year compressive strength. However the multivariable relationships using $(C_3A)^2$ or $(C_3A)^3$ together with the compressive strengths at the various ages (equations 16 through 30 and 46 through 60) present evidence to the effect that the compressive strength at the early ages (1, 3, and 7 days) may be associated with a reduction in the sulfate expansion values. (The "F" values for these equations were in each case over 200 primarily because of the inclusion of the C_3A as one of the independent variables.)

The coefficient/s.d. ratio for 1-, 3-, and 7-day strength ranged from about 1.0 to 2.0 for the different combinations which does not indicate a highly significant effect. In these equations (16 through 30 and 46 through 60) the coefficients for compressive strength were highest with the 1-day strength and were successively lower when the strength at later ages was used as an independent variable. The sign of the coefficients was in each instance minus and in this respect consistent with the effect that high C_3S cements (normally associated with high early strength) also were associated with low expansion of the mortar prisms.

Both Federal and ASTM specifications at one time limited the amount of potential C_3S permitted in the Type V sulfate resisting cements, but this limitation was later removed. The proposed test [5] which is of short duration indicates that a high C_3S content is desirable. Miller et al. [1], quoted a number of references (No. 90, 98, 100, 351, 354, 357, 361, and 398 for example) which indicated that cements with high lime content or C_3S are more susceptible to certain types of sulfate attack than cements with low C_3S content. Lea and Desch [3, page 299], have indicated that C_3S expands rapidly in magnesium sulfate solution and very slowly in sodium or calcium sulfate solution. The use of calcium sulfate as in the present study and in the proposed ASTM test for potential sulfate expansion [5] may, therefore, not properly evaluate the resistance of portland cements where magnesium sulfate as present in sea water contributes to the deleterious reactions. On the other hand, it appears well established that high-quality concretes made with sufficient cement and low water-cement ratio as well as adequate curing or autoclaving prior to exposure to sulfate solutions have superior sulfate resistance. Other factors being equal, high C_3S cements tend to form their hydration products more rapidly and would require less curing time to attain the degree of hydration and impermeability necessary for resistance to attack by sulfate solutions.

There is a great deal of evidence in the literature to the effect that the use in concrete of finely ground silica and other pozzolanic materials tends, as a general rule, to improve the resistance to sulfate attack. This improved resistance has been attributed to the reaction of the pozzolans with calcium hydroxide, a product of the hydration of C_3S, but may also result from the enhanced impermeability of the concrete.

TABLE 4–18. *Coefficients for equations relating the sulfate expansion at various ages to strength and C_3A content of 1 to 15 percent*

Equation	Type cement	Note	Const.	Str (1d)	Str (3d)	Str (7d)	Str (28d)	Str (1yr)	$(C_3A)^2$	$(C_3A)^3$	S.D.	"F"**
1	AE+NAE	(1)	SE_{14}=+0.0460 s.d.= (0.0045)	*−0.0000014 (0.0000043)							0.0216	0.05
2	do	(1)	SE_{14}=+0.0381 s.d.= (0.0053)		+0.0000024 (0.0000023)						0.0215	0.54
3	do	(1)	SE_{14}=+0.0328 s.d.= (0.0053)			+0.0000032 (0.0000017)					0.0214	1.67
4	do	(1)	SE_{14}=+0.0445 s.d.= (0.0096)				*−0.0000002 (0.0000019)				0.0216	0.01
5	do	(1)	SE_{14}=+0.1111 s.d.= (0.0110)					−0.000011 (0.000002)			0.0195	19.6
6	do	(2)	SE_{28}=+0.0647 s.d.= (0.0077)	*−0.0000015 (0.0000073)							0.0371	0.02
7	do	(2)	SE_{28}=+0.0525 s.d.= (0.0090)		+0.0000050 (0.0000040)						0.0369	0.78
8	do	(2)	SE_{28}=+0.0437 s.d.= (0.0102)			+0.0000060 (0.0000030)					0.0366	2.01
9	do	(2)	SE_{28}=+0.0636 s.d.= (0.0164)				*−0.00000008 (0.00000320)				0.0371	0.00
10	do	(2)	SE_{28}=+0.1777 s.d.= (0.0189)					−0.000018 (0.000003)			0.0335	18.7
11	do	(3)	SE_{84}=+0.1445 s.d.= (0.0259)	*−0.000012 (0.000025)							0.1243	0.11
12	do	(3)	SE_{84}=+0.1075 s.d.= (0.0304)		*+0.000012 (0.000013)						0.1241	0.40
13	do	(3)	SE_{84}=+0.0835 s.d.= (0.0343)			+0.000015 (0.000010)					0.1235	1.14
14	do	(3)	SE_{84}=+0.1495 s.d.= (0.0550)				*−0.000003 (0.000011)				0.1243	0.05
15	do	(3)	SE_{84}=+0.4989 s.d.= (0.0640)					−0.000059 (0.000010)			0.1136	16.7
16	do	(1)	SE_{14}=+0.0213 s.d.= (0.0027)	−0.0000046 (0.0000023)					+0.00033 (0.00002)		0.0116	>100
17	do	(1)	SE_{14}=+0.0215 s.d.= (0.0030)		−0.0000023 (0.0000013)				+0.00033 (0.00002)		0.0116	>100
18	do	(1)	SE_{14}=+0.0225 s.d.= (0.0033)			−0.0000019 (0.0000010)			+0.00033 (0.00002)		0.0116	>100
19	do	(1)	SE_{14}=+0.0258 s.d.= (0.0052)				−0.0000018 (0.0000010)		+0.00033 (0.00002)		0.0116	>100
20	do	(1)	SE_{14}=+0.0194 s.d.= (0.0085)					*−0.0000004 (0.0000012)	+0.00032 (0.00002)		0.0118	>100

21	do	[2]	SE_{28}=+0.0245 s.d.= (0.0045)	−0.0000071 (0.0000039)					+0.00057 (0.00003)		0.0197	>100
22	do	[2]	SE_{28}=+0.0240 s.d.= (0.0050)		−0.0000032 (0.0000022)				+0.00057 (0.00003)		0.0197	>100
23	do	[2]	SE_{28}=+0.0258 s.d.= (0.0055)			−0.0000027 (0.0000017)			+0.00057 (0.00003)		0.0197	>100
24	do	[2]	SE_{28}=+0.0313 s.d.= (0.0089)				−0.0000027 (0.0000017)		+0.00057 (0.00003)		0.0197	>100
25	do	[2]	SE_{28}=+0.0179 s.d.= (0.0144)					*+.00000002 (0.00000206)	+0.00056 (0.00003)		0.0199	>100
26	do	[3]	SE_{84}=+0.0459 s.d.= (0.0146)	−0.000024 (0.000013)						+0.000130 (0.000006)	0.0661	>100
27	do	[3]	SE_{84}=+0.0456 s.d.= (0.0165)		−0.000011 (0.000007)					+0.000131 (0.000006)	0.0663	>100
28	do	[3]	SE_{84}=+0.0521 s.d.= (0.0184)			−0.0000094 (0.0000055)				+0.000132 (0.000006)	0.0682	>100
29	do	[3]	SE_{84}=+0.0580 s.d.= (0.0298)				−0.0000069 (0.0000057)			+0.000129 (0.000006)	0.0665	>100
30	do	[3]	SE_{84}=+0.0019 s.d.= (0.0467)					*+0.0000032 (0.0000069)		+0.000131 (0.000007)	0.0667	>100
31	NAE	[4]	SE_{14}=+0.0423 s.d.= (0.0046)	*−0.00000017 (0.00000431)							0.0211	0.00
32	do	[4]	SE_{14}=+0.0346 s.d.= (0.0054)		+0.0000034 (0.0000023)						0.0210	1.07
33	do	[4]	SE_{14}=+0.0286 s.d.= (0.0061)			+0.0000041 (0.0000018)					0.0207	2.68
34	do	[4]	SE_{14}=+0.0332 s.d.= (0.0103)				*+0.0000017 (0.0000020)				0.0210	0.39
35	do	[4]	SE_{14}=+0.1112 s.d.= (0.0129)					−0.0000109 (0.0000020)			0.0194	14.5
36	do	[5]	SE_{28}=+0.0613 s.d.= (0.0078)	*+0.00000015 (0.00000737)							0.0361	0.00
37	do	[5]	SE_{28}=+0.0470 s.d.= (0.0092)		+0.0000066 (0.0000040)						0.0358	1.35
38	do	[5]	SE_{28}=+0.0368 s.d.= (0.0104)			+0.0000074 (0.0000030)					0.0354	3.01
39	do	[5]	SE_{28}=+0.0454 s.d.= (0.0176)				*+0.0000031 (0.0000034)				0.0360	0.43
40	do	[5]	SE_{28}=+0.1787 s.d.= (0.0221)					−0.000019 (0.000003)			0.0332	14.3
41	do	[6]	SE_{84}=+0.1333 s.d.= (0.0264)	*−0.0000036 (0.0000249)							0.1221	0.01
42	do	[6]	SE_{84}=+0.0905 s.d.= (0.0314)		+0.000018 (0.000014)						0.1214	0.86
43	do	[6]	SE_{84}=+0.0619 s.d.= (0.0354)			+0.000020 (0.000010)					0.1206	1.97
44	do	[6]	SE_{84}=+0.1046 s.d.= (0.0596)				*+0.0000049 (0.0000115)				0.1220	0.09

See footnotes at end of table (page 22).

Continued on page 22.

TABLE 4–18. *Coefficients for equations relating the sulfate expansion at various ages to strength and C_3A content of 1 to 15 percent*—Continued

Equation	Type cement	Note	Const.	Str (1d)	Str (3d)	Str (7d)	Str (28d)	Str (1yr)	$(C_3A)^2$	$(C_3A)^3$	S.D.	"F"**
45	AE+NAE	[6]	SE_{84}=+0.5386 s.d.= (0.0743)					−0.000065 (0.000012)			0.1116	15.4
46	do	[4]	SE_{14}=+0.0212 s.d.= (0.0029)	−0.0000042 (0.0000024)					+0.00032 (0.00002)		0.0117	>100
47	do	[4]	SE_{14}=+0.0212 s.d.= (0.0031)		−0.0000020 (0.0000013)				+0.00032 (0.00002)		0.0117	>100
48	do	[4]	SE_{14}=+0.0220 s.d.= (0.0034)			−0.0000016 (0.0000010)			+0.00032 (0.00002)		0.0117	>100
49	do	[4]	SE_{14}=+0.0234 s.d.= (0.0057)				−0.0000012 (0.0000011)		+0.00032 (0.00002)		0.0117	>100
50	do	[4]	SE_{14}=+0.0106 s.d.= (0.0099)					*+0.000010 (0.0000014)	+0.00032 (0.00002)		0.0117	>100
51	do	[5]	SE_{28}=+0.0250 s.d.= (0.0047)	−0.0000067 (0.0000040)					+0.00055 (0.00003)		0.0197	>100
52	do	[5]	SE_{28}=+0.0241 s.d.= (0.0052)		−0.0000027 (0.0000023)				+0.00055 (0.00003)		0.0198	>100
53	do	[5]	SE_{28}=+0.0257 s.d.= (0.0058)			−0.0000024 (0.0000018)			+0.00056 (0.00003)		0.0197	>100
54	do	[5]	SE_{28}=+0.0284 s.d.= (0.0097)				−0.0000020 (0.0000019)		+0.00055 (0.00003)		0.0198	>100
55	do	[5]	SE_{28}=+0.0051 s.d.= (0.0167)					*+0.0000020 (0.0000024)	+0.00056 (0.00003)		0.0198	>100
56	do	[6]	SE_{84}=+0.0438 s.d.= (0.0151)	−0.000020 (0.000014)						+0.000128 (0.000007)	0.0663	>100
57	do	[6]	SE_{84}=+0.0426 s.d.= (0.0173)		−0.0000085 (0.0000076)					+0.000128 (0.000007)	0.0664	>100
58	do	[6]	SE_{84}=+0.0483 s.d.= (0.0195)			−0.0000076 (0.0000059)				+0.000130 (0.000007)	0.0664	>100
59	do	[6]	SE_{84}=+0.0543 s.d.= (0.0326)				*−0.0000058 (0.0000063)			+0.000128 (0.000007)	0.0665	>100
60	do	[6]	SE_{84}=+0.0108 s.d.= (0.0550)					*+0.0000053 (0.0000081)		+0.000130 (0.000008)	0.0666	>100

[1] 170 cements, avg 0.0433, S.D.=0.0215. [2] 170 cements, avg 0.0632, S.D.=0.0370. [3] 170 cements, avg 0.1333, S.D.=0.1240. [4] 159 cements, avg 0.0422, S.D.=0.0210. [5] 159 cements, avg 0.0614, S.D.=0.0360. [6] 159 cements, avg 0.1297, S.D.=0.1217. *Coef./s.d. less than 1. **Critical limit, 3.05 for α=0.05, 2:168 degrees of freedom for AE+NAE and 2:157 for NAE cements.

Portland-blast-furnace-slag cements have, according to many references, a good record with respect to sulfate resistance in service. Cements of this class, having somewhat lower strengths at early ages, tend to have high expansion values when tested by the methods used in this study. For example, using the same test procedures as for the portland cements, tests were also made on seven commercial portland-blast-furnace-slag cements. The average 14-day expansion was 0.093 percent. All of these cements had 14-day expansion values greater than the 0.045 percent limit which has been proposed and one of the cements had a 14-day expansion value of 0.133 percent.

In determining the variables associated with the expansion at the various ages of the prisms made of the different cements, a large number of equations were computed. The equations presented in this section were selected because of their relevancy to the problem. Advantage was taken of supplementary statistical tests previously described [10] to determine which of the available independent variables were possible contributors to the deviations between observed and calculated values. The final criterion was the behavior of these variables in the multiple regression equations. It seems unlikely therefore that any independent variable not used in the respective equations could have a major effect on the relationship presented.

In the computations of the multivariable relationships the potential C_3A or some power of the C_3A was usually used as one of the independent variables in each of the series of equations. However, it was also demonstrated that the Al_2O_3 content of the cement could be used as an independent variable providing other significant variables were also employed, and this resulted in equally good agreement between the observed and calculated expansion. Similarly the potential C_3S was used in some instances, whereas the CaO/SiO_2 ratio was used in most of the equations. With a given Fe_2O_3 content the amount of C_3S as calculated would increase with the increase in the CaO/SiO_2 ratio. The Fe_2O_3 was used rather than the C_4AF because of the fact that the C_4AF is computed as a constant times the Fe_2O_3 content for the range of Fe_2O_3 present in these cements.

For the cements having 0 to 9 percent C_3A, expansion increased with increasing Fe_2O_3, loss on ignition, and K_2O of the commonly determined variables (in addition to C_3A), while it decreased with increasing CaO/SiO_2 and insoluble residue. The effect of these commonly determined variables other than C_3A appeared to decrease with age at which measurements were made, i.e., the coefficients were closer to zero at the later ages. Other independent variables such as SrO, Cu, V, Zn, and Ni also appeared to be associated with the expansion of these cements. Of these trace elements, Cu was the only element associated with low expansion values. V and Zn appeared to be associated with high expansion values at 14 days (although coefficient/s.d. for Zn is not significantly large), whereas Ni appeared associated with the expansion values at the later ages. The coefficient/s.d. ratios of the individual trace elements were not highly significant but it appears that further studies by other means are warranted. The limitations of the analyses by methods employed in this section have been discussed in a previous section [10].

Whereas plots and computations of the multivariable relationships indicated that the use of linear relationships appeared adequate for cements having 0 to 9 percent C_3A, this was not true for the group of cements having 7 to 15 percent C_3A, where lower S.D. values were obtained when using the second or third power of the C_3A contents of the cements. For cements having 7 to 15 percent C_3A the coefficient for Fe_2O_3 was negative, with a high coefficient/s.d. ratio at all three ages, whenever C_3A was not included as a variable, indicating that expansion decreased with increasing Fe_2O_3 content. When C_3A was used as a variable instead of Al_2O_3, however, the coefficient of Fe_2O_3 was not significant in most cases. This apparent anomaly results from the method used in computing the potential compound composition [8] in which the Fe_2O_3 is assumed to require an amount of Al_2O_3 sufficient to form the C_4AF in those cements having a high Al_2O_3 content.

With this group of cements and the variables used, high values of CaO/SiO_2 were associated with low expansion values. Whereas the loss on ignition may be significant at 14 days, the coefficient/s.d. ratio was less than one at the later ages. The insoluble residue and K_2O contents were apparently not associated with the expansion of these cements as with the cements of low C_3A content. Of the minor constituents and trace elements, SrO appeared significant at 14 days but not at later ages. P appeared significant at the later ages, although statements about this element are doubtful because of the few cements which had a measurable amount. Cr and V also appeared to be associated with the expansion values. Cr_2O_3 and P_2O_5 are both included with the Al_2O_3 in the usual chemical analyses of portland cements unless the Al_2O_3 is corrected for these oxides. Unless such corrections are made, their presence will detract from the accuracy of the calculated potential C_3A content. It is of interest to note, however, that in the computations in this article the sign of the coefficient for P is minus and for Cr it is plus. Hence it would appear that their presence in the equation is not primarily as a correction for the lack of accuracy of the Al_2O_3 and/or the C_3A content. Although the Cr values reported appeared to present a reasonable distribution of values in the different cements, P which is believed present in minor quantities in most portland cements was reported only for those cements having 0.1 percent or more P as determined by the spectrochemical method. More refined procedures than those employed in the present study will be

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required to verify the effect of the trace elements on the sulfate expansion as measured by the potential sulfate expansion test or in determining the effect, if any, on the susceptibility to sulfate attack of concretes containing varying amounts of these elements.

In comparing the equations computed for the AE+NAE cements with those computed for the NAE cements only slight differences were noted in the magnitude of the coefficients or the coefficient/s.d. ratios. However, there were only 5 air-entraining cements in the 0 to 9 percent C_3A group and 11 air-entraining cements in the 7 to 15 percent C_3A group on which the computations were made. Because of the relatively few air-entraining cements in each of the groups, it was of no value to compute multivariable regression equations for these cements by themselves.

Computations were made comparing the observed values for expansion of the mortar prisms of the cements common to both the 0 to 9 and 7 to 15 percent C_3A versus the values computed by the equations for the respective groups. These studies indicated that the computed expansion values for cements having 7 to 9 percent C_3A were more in accord with the observed values when using the equations developed for the group of cements having 0 to 9 percent C_3A.

It was pointed out in part 1, section 1 of this series of articles that limitations of the ranges of certain variables made the task of evaluating the true effect of such variables more difficult. If, however, a group of cements used in an equation includes one with very unusual properties, this one cement may affect not only the ratios of coefficients to s.d. values of the other variables, but also the S.D. value of the equation. An example of such an effect is presented in table 4–19. Five pairs of equations were computed for cements containing 7 to 15 percent C_3A with and without a cement which, as previously noted, had a high autoclave expansion. It may be noted that the coefficient/s.d. ratios with this cement excluded were less than one in many instances where the coefficients with it were of marginal significance. The S.D. values of equations without this cement were lower than in corresponding equations where it was included. All of the cements other than the one cited above had low autoclave expansion values which indicated that the free calcum oxide contents were very low. Because of this and the questionable significance of very small values of free calcium oxide as determined by available methods, no analyses were made of this constituent. This variable may have been one of the many unknown factors contributing to the lack of better agreement between the computed and determined expansion values.

8. Summary and Conclusions

Studies were made of the relationship of cement composition to the expansion of mortar bars in the test for potential sulfate resistance of portland cements. In this test sufficient molding plaster was added to the cement to make the SO_3 content 7.0 percent. Measurements were made at 14, 28, and 84 days of the expansion of 1:2.75 (cement plus $CaSO_4$ to graded Ottawa sand) mortar bars made of 183 portland cements of different types having a normal range of chemical compositions.

Plots of the expansions of the mortar bars versus age after fabrication indicated that up to 2 or 3 months there were few cements which changed their relative rating in the group of cements. Somewhat greater differences in the expansion values were obtained at 28 days than at 14 days which afforded a better discrimination between the cements. At later ages the prisms made from some of the cements of medium or high C_3A content warped or deteriorated, making measurements after three months of questionable value.

Plots of the expansion values of the prisms made of the different cements versus the C_3A content of the cements indicated a general relationship. Plots of the expansion values of the different cements versus other variables indicated to some extent the independent variables associated with the cements having high or low expansion values.

Multivariable relationships were computed by a least squares method of the relationship of the expansion values of the mortar bars at the different ages and various combinations of independent variables. The computations of the equations were made on cements having 0 to 9 percent potential C_3A and on cements having 7 to 15 percent potential C_3A. Whereas a linear relationship appeared adequate for the low C_3A cements, the use of the second or third power of the C_3A in the high C_3A cements resulted in better agreement between the observed expansion values and those computed by the equations. In addition to the potential C_3A content of the cement, other commonly determined variables associated with high expansion values for the low C_3A cements were as follows: high values for the Fe_2O_3, loss on ignition, and K_2O; and low values of the CaO/SiO_2 ratio and insoluble residue. The effect of these variables decreased with the increase in the age at which the expansion measurements were made. Other independent variables such as SrO, Cu, V, Zn, and Ni were also associated with the expansion of the prisms. Cu was the only one of these trace elements for which high values were associated with low expansion values of the prisms. The calulated contribution of the trace elements to the expansion values increased with the age at which expansion measurements were made.

For cements having high C_3A values, high values for Fe_2O_3 and CaO/SiO_2 were associated with the cements having low expansion values for

TABLE 4-19. *Coefficients for equations relating the 14-day sulfate expansion of cements with 7 to 15 percent C_3A to various independent variables*

Equation	Type cement	Note	Const.	C_3A	Fe_2O_3	$\frac{CaO}{SiO_2}$	Insol.	Loss	MgO	SrO	Cu	V	S.D.	F
1A	AE+NAE	(1)	SE_{14}=−0.0260 s.d.= (0.0066)	+0.0077 (0.0006)									0.0154	1.23
1B	do	(2)	SE_{14}=−0.0223 s.d.= (0.0060)	+0.0073 (0.0006)									0.0139	
2A	do	(1)	SE_{14}=+0.0588 s.d.= (0.0317)	+0.0096 (0.0009)	+0.0085 (0.0026)	−0.0457 (0.0131)	+0.0255 (0.0094)	+0.0036 (0.0025)	−0.0019 (0.0012)				0.0140	1.13
2B	do	(2)	SE_{14}=+0.0639 s.d.= (0.0299)	+0.0094 (0.0008)	+0.0064 (0.0026)	−0.0446 (0.0124)	*+0.0061 (0.0102)	+0.0047 (0.0024)	*−0.0009 (0.0012)				0.0132	
3A	do	(1)	SE_{14}=+0.0654 s.d.= (0.0318)	+0.0100 (0.0009)	+0.0098 (0.0027)	−0.0472 (0.0130)	+0.0246 (0.0092)	*+0.0016 (0.0027)	−0.0023 (0.0013)	−0.0179 (0.0144)	−0.2735 (0.2479)	−0.2602 (0.1523)	0.0137	1.09
3B	do	(2)	SE_{14}=+0.0702 s.d.= (0.0303)	+0.0097 (0.0009)	+0.0077 (0.0027)	−0.0462 (0.0124)	*+0.0069 (0.0101)	+0.0029 (0.0026)	−0.0014 (0.0012)	*−0.0113 (0.0139)	−0.2463 (0.2358)	−0.2204 (0.1464)	0.0131	
4A	do	(1)	SE_{14}=+0.0642 s.d.= (0.0317)	+0.0099 (0.0009)	+0.0098 (0.0027)	−0.0456 (0.0127)	+0.0261 (0.0089)		−0.0024 (0.0012)	−0.0184 (0.0144)	−0.2756 (0.2471)	−0.2931 (0.1429)	0.0137	1.09
4B	do	(2)	SE_{14}=+0.0678 s.d.= (0.0303)	+0.0095 (0.0009)	+0.0078 (0.0027)	−0.0435 (0.0122)	+0.0105 (0.0097)		−0.0018 (0.0012)	*−0.0124 (0.0139)	−0.2514 (0.2361)	−0.2817 (0.1365)	0.0131	
5A	do	(1)	SE_{14}=+0.0601 s.d.= (0.0319)	+0.0103 (0.0009)	+0.0085 (0.0027)	−0.0492 (0.0134)		+0.0060 (0.0024)					0.0144	1.21
5B	do	(2)	SE_{14}=+0.0621 s.d.= (0.0291)	+0.0095 (0.0008)	+0.0062 (0.0025)	−0.0448 (0.0122)		+0.0053 (0.0022)					0.0131	

[1] 114 cements, avg=0.0529, S.D.=0.0234; high autoclave expansion cement included. [2] 113 cements, avg=0.0521, S.D.=0.0216; high autoclave expansion cement not included. *Coefficient/s.d. less than 1.

TABLE 4-20. *"F" values for significance of reduction of variance due to added variables*

Table	Equations	"F" ratio	D.F.	Critical "F" ratio	
				α=0.01	α=0.05
4-4	1, 4	16.2	5:97	3.22	2.32
	4, 5	3.7	4:93	3.53	2.45
	6, 7	3.9	4:93	3.53	2.45
	8, 11	16.3	5:92	3.22	2.32
	11, 12	3.8	4:88	3.52	2.48
	13, 14	3.7	4:88	3.54	2.48
4-6	1, 4	11.8	5:97	3.22	2.32
	4, 6	4.2	3:94	4.00	2.71
	10, 12	4.3	3:94	4.00	2.71
	14, 17	11.7	5:92	3.22	2.32
	17, 19	4.1	3:89	4.02	2.72
	23, 25	4.1	3:89	4.02	2.72
4-8	1, 6	7.0	5:97	3.22	2.32
	2, 7	8.6	5:97	3.22	2.32
	6, 8	5.6	3:94	4.00	2.21
	7, 9	4.7	3:94	4.00	2.21
	12, 17	6.4	5:92	3.22	2.31
	17, 19	5.5	3:89	4.02	2.71
4-10	1, 3	5.1	3:108	3.97	2.69
	1, 4	4.2	5:106	3.18	2.30
	5, 6	2.7	3:105	3.98	2.70
	7, 9	4.6	3:97	4.00	2.70
	7, 10	4.2	5:95	3.22	2.31
	11, 12	2.5	3:94	4.00	2.71
4-12	1, 3	3.9	1:110	6.87	3.93
	3, 4	11.3	3:107	3.97	2.70
	10, 11	16.7	2:109	4.83	3.08
	11, 12	11.1	3:106	3.98	2.70
	14, 16	2.7	1:99	6.90	3.93
	16, 17	10.0	3:96	4.00	2.71
	23, 24	14.8	2:98	4.83	3.08
	24, 25	9.9	3:95	4.00	2.71
4-14	1, 3	5.0	1:110	6.87	3.93
	3, 4	9.2	3:107	3.97	2.70
	8, 9	21.0	2:109	4.81	3.08
	9, 10	6.6	3:106	3.98	2.70
	11, 13	4.5	1:99	6.90	3.99
	13, 14	10.2	3:96	4.00	2.71
	18, 19	19.5	2:98	4.83	3.08
	19, 20	5.8	3:95	4.00	2.71

the prisms at all ages. Of the minor or trace elements, SrO, Cr, V, and P appeared to be associated with the expansion values, the SrO at 14 days, and the P at later ages. The calculated contribution of the trace elements (other than SrO) increased with the age at which the expansion measurements were made.

The observed and computed values of the expansions of cements having 7 to 9 percent C_3A were in better agreement when the equations computed for 0 to 9 percent C_3A cements were used when the equations for the 7 to 15 percent C_3A cements were used.

The use of the products of the autoclave-expansion values and MgO and C_3A contents of the cements, respectively, as additional independent variables in the equations resulted in lower S.D. values for the low C_3A cements but not for cements having high C_3A contents.

The difference between determined values and those computed from the equations as indicated by the standard deviation values of the best equations were larger than the standard deviation values of duplicate determinations made on a different group of cements in a supplementary series of tests, but no more than would be expected in view of the larger error that would be found with a large number of tests spread over a comparatively large period of time as compared to that obtained from duplicate tests run close together. However, a need is still indicated for further study to determine the additional variables which may be involved in the test for potential sulfate expansion of cements.

Regression lines computed to determine the relationship of the expansion values of the cements to the compressive strengths of the 1:2.75 (cement to standard Ottawa sand) mortar cubes indicated that the expansion values obtained were not associated with the compressive strength alone at the early ages but were related to the compressive strength at one year. However, if a function of the C_3A was included as an independent variable, a relationship between the strength of the mortars and the expansion appeared, the cements with high compressive strength values being associated with those cements having low expansion values.

In conclusion it would appear that, in view of the highly significant relationships existing not only for the potential C_3A content, but for other commonly determined variables together with the relationship of certain trace elements to the sulfate expansion values obtained in the test for potential sulfate resistance of portland cements, further studies are warranted and desirable to determine the possible effect of such variables on the susceptibility of concretes exposed to sulfate attack.

In addition to the acknowledgements indicated in previous sections in this series of articles, special acknowledgements are made to M. R. DeFore and A. C. Figlia, who conducted most of the tests, and to Paul Worksman for studies of the reproducibility of the expansion values at various ages.

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Section 5. Heat of Hydration of Portland Cements

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The relationships between the chemical characteristics of portland cements and the heat of hydration at 7 and 28 days and at 1 year were studied by computing multivariable regression equations with the aid of a digital computer and determining which of the independent variables appeared to have a significant relationship to the heat of hydration values. The computed equations verified to a reasonable degree effects usually attributed to the major potential compounds. Other commonly determined variables, such as fineness and loss on ignition, were associated with the heat of hydration at all ages; K_2O and SO_3 with the 7 day; and Na_2O with the 1-year heat of hydration. Of the other minor constituents Cu and P appeared to be associated with the heat of hydration at all ages. In addition, Cr and Zr were associated with heat of hydration at 7 days; Co, Zr, and SrO at 28 days; and V and Ba at 1 year.

Contents

1. Introduction

The heat of hydration of portland cements has been dealt with rather extensively in books by Lea and Desch [1] [1], Bogue [2], and Taylor [3] as well as by different authors in the "Proceedings" of the London [4] and Washington [5] symposia on the chemistry of cement. The values reported by Lerch and Bogue [6] as well as Thorvaldson, Brown, and Peaker [7] on compounds hydrated independently; and the values obtained by least squares analyses and reported by Woods, Steinour, and Starke [8]; Davis, Carlson, Troxell, and Kelly [9]; and Verbeck and Foster [10] have also been widely quoted. Generally, the heat of hydration determined by the heat of solution method has been evaluated statistically in relation to the potential compounds or major oxides present in portland cement. However, studies have also been made of its relationship to other factors such as fineness and rate of cooling of clinker [11], water-cement ratio [12], and curing temperature and loss on ignition [13], all of which may have an appreciable effect on the heat of solution values. Schwiete and Tan Tik-Ien [14] have demonstrated that other oxides such as MgO and Al_2O_3 incorporated in the tricalcium silicate phase have an effect on the heat of solution values. Other elements are also known to act as "stabilizers" for some of the potential compounds and are believed to affect the hydration process. Although Copeland and Kantro [15] and Verbeck [16] have summarized studies by many investigators on the heat of hydration of cements, no comprehensive literature is available on the effect of minor constituents. This section of the series on the Interrelations Between Cement and Concrete Properties deals, therefore, not only with the effects of potential compound composition and major oxides on the heat of hydration, but also with the effect of the minor and trace elements.

[1] Figures in brackets indicate the literature references at the end of this section.

2. Materials and Test Methods

The portland cements used in this series of tests have been described in sections, 1 and 3 of part 1, dealing with Materials and Techniques [17] and Occurrence of Minor and Trace Elements [18]. As indicated in these previous sections, the cements were procured from different areas of the United States with only a few from other countries. The different cements were classified into different types, primarily on the basis of their chemical composition. The heat of hydration values were not taken into consideration at the time the cements were so classified.

The heat of hydration values were determined at 7 and 28 days and 1 year by the heat of solution method described in Federal [19] and ASTM [20] specifications. The 7- and 28-day tests were made on most but not all of the portland cements whereas the 1-year tests were made on slightly more than half the cements. Duplicate tests were made on most of the cements tested. All tests were conducted at the Seattle laboratory of the National Bureau of Standards under the supervision of F. N. Winblade and G. Watton.

The notations HH(7), HH(28), and HH(1Y) are used in this section to designate the heat of hydration at 7 days, 28 days, and 1 year respectively. Other commonly used notations and abbreviations have been presented in section 1 [17].[2]

3. Statistical Analyses

The statistical techniques used to determine the independent variables associated with the heat of hydration values have been described in a previous section of this series on Materials and Techniques [17]. These techniques included plots of the dependent and major independent variables as well as the use of the "tic-tac-toe" and the Student's "t" test of the "hi-lo" and "middle ends" variations to determine which of the minor constituents or trace elements were probable contributing factors to variations. The equations obtained by the least squares method (tables 5–2, 5–3, 5–6, 5–7, 5–10, 5–11, and 5–14) were the most important means of drawing conclusions. As in previous sections, comparisons were made of the degree of fit using only major constituents, these with commonly detemined variables and these together with the minor or trace elements. Equations were also computed for the "odds" and "evens" in the array of cements. Abbreviations employed in previous sections are also used in this section.[3] In addition "F" values for the reduction in variance due to added variables in a number of pairs of equations are given in table 5–13.

In calculations of the least squares equations three white cements and a cement with high autoclave expansion were eliminated from consideration. Certain other cements reported had heat of solution values which consistently showed excessively large deviations in preliminary equations, and these were also eliminated in the final equations. No reason was apparent for their nonconformance.

Most authors indicated by previous references [1 through 10] have assumed that the heats of hydration of the potential compounds in portland cement are additive and that relationships between heat of hydration and constituents are essentially linear and pass through the origin. In this study some equations were computed both with and without a constant term. The constants, when calculated, did not differ statistically from zero (i.e., the s.d. of the constant was large in relation to the constant) and the assumption of a zero constant appeared to be most consistent with known facts regarding the hydration of cement compounds. Therefore, no constants are used in the equations presented in this section.

4. Results of Tests

4.1. Plots of Heat of Hydration Versus Independent Variables

In figure 5–1 are presented the results of plotting the heat of hydration values at the three ages versus various independent variables. The procedure for dividing the values into 12 groups, plotting of the points, separating into quadrants and evaluating the relationship on the basis of the number and position of the points in the four quadrants has previously been discussed (see sec. 1 [17]). As previously indicated [17] an absolute value of 11 or greater in the line "note 4" can be considered significant at the 95 percent level. It may be noted that SiO_2, Al_2O_3, Fe_2O_3, and SO_3 met this requirement at each of the three ages. K_2O and total

[2] The notations C_3A, C_3S, C_2S, and C_4AF are used as is customary in cement technology for the potential tricalcium aluminate, tricalcium silicate, dicalcium silicate, and tetracalcium aluminoferrite, respectively. The terms A/F and S/(A+F) refer to the ratios of Al_2O_3, Fe_2O_3, and SiO_2. Also used are Loss for loss on ignition and APF for air-permeability fineness. AE is used to designate the air-entraining cements and NAE for the non-air-entraining cements.

[3] Among the statistical terms used in this and other sections of this series are the following:
- S.D.=Standard deviation calculated from the residuals of a fitted equation, or the standard deviation about the average.
- s.d.=Estimated standard deviation of the coefficient of an individual independent variable when used in a fitted equation.
- Coef./s.d. or Coefficient/s.d.=Ratio of the estimated coefficient (of an independent variable used in an equation) to its estimated standard deviation.
- *"F"*=Fisher's ratio of variance estimates. Critical *"F"* values were obtained from tables presented in most textbooks on statistics.

HEAT OF HYDRATION	INDEPENDENT VARIABLES																	
AGE	NOTE	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TOTAL Alkali	C_3A	C_3S	C_2S	C_4AF	$\frac{A}{F}$	$\frac{S}{A+F}$	Air p. Fine.	Wagn. Fine
7 DAY	(1)	$\frac{10}{2}$	$\frac{12}{0}$	$\frac{12}{0}$	$\frac{10}{2}$	$\frac{6}{6}$	$\frac{10}{2}$	$\frac{7}{3}$	$\frac{10}{2}$	$\frac{10}{2}$	$\frac{12}{0}$	$\frac{10}{2}$	$\frac{12}{0}$	$\frac{12}{0}$	$\frac{12}{0}$	$\frac{10}{2}$	$\frac{10}{2}$	$\frac{6}{6}$
	(2)																	
	(3)	NL	L	L	L?	NO	L	NO	L	L	L	L	L	L	L	NL	NL	NO
	(4)	−18	+24	−24	+12	+3	+15	+2	+17	+15	+24	+12	−24	−24	+24	−14	+10	+1
28 DAY	(1)	$\frac{12}{0}$	$\frac{12}{0}$	$\frac{12}{0}$	$\frac{10}{2}$	$\frac{6}{6}$	$\frac{12}{0}$	$\frac{8}{4}$	$\frac{8}{4}$	$\frac{6}{6}$	$\frac{12}{0}$	$\frac{10}{2}$	$\frac{12}{0}$	$\frac{12}{0}$	$\frac{12}{0}$	$\frac{10}{2}$	$\frac{10}{2}$	$\frac{6}{6}$
	(2)																	
	(3)	NL	L	L	NL	NO	L	NO	L?	NO	L	L	L	L	L	NL	NL	NO
	(4)	−24	+24	−24	+9	0	+24	−4	+8	+5	+24	+17	−24	−24	+24	−14	+17	+1
1 YEAR	(1)	$\frac{10}{2}$	$\frac{12}{0}$	$\frac{12}{0}$	$\frac{8}{4}$	$\frac{6}{6}$	$\frac{10}{2}$	$\frac{6}{6}$	$\frac{8}{4}$	$\frac{8}{4}$	$\frac{12}{0}$	$\frac{10}{2}$	$\frac{10}{2}$	$\frac{10}{2}$	$\frac{12}{0}$	$\frac{10}{2}$	$\frac{8}{4}$	$\frac{8}{4}$
	(2)																	
	(3)	L	L	L	L	NO	L	NO	L?	L?	L	L	L	L	L	NO	L?	NO
	(4)	−19	+24	−18	+11	+1	+17	−4	+8	+1	+24	+17	−18	−17	+24	−17	+6	0

FIGURES 5–1. *Results of plotting heat of hydration at 7 days, 28 days, and 1 year on the "y" axis versus various independent variables on the "x" axis.*

Note 1, ratio of plotted points occurring in pairs of diametrically opposite quadrants.
Note 2, general trend of line drawn through the plotted points.
Note 3, apparent nature of the relationship, —L=linear, NL=non-linear, NO=no apparent relationship, and N?=not determinable.
Note 4, quadrant sum (see Part 1, section 1 of this series of papers).

alkali had a quadrant sum greater than 11 only for the 7 day tests, whereas Na_2O showed no significant relationship at any of the ages at which the tests were made. The relationships of C_3A, C_3S, C_2S, and C_4AF to heat of hydration were highly significant at all ages, but the slopes of both C_2S and C_4AF were negative. This probably results from the predominant effect of C_3A and C_3S. As the Fe_2O_3 increases, the C_4AF increases and the C_3A decreases. Also, as the amount of C_3S in portland cement increases, the amount of C_2S generally decreases. The A/F and S/(A+F) ratios have highly significant relationships to the heat of hydration values with the latter having a negative slope. The effect of fineness, especially as determined by the turbidimeter method, was apparently masked by the other more important variables.

4.2. Heat of Hydration at 7 Days

The frequency distributions of the 7-day heat of hydration values of the cements of the different types are presented in table 5–1. Each of the types of cement (classified on the basis of chemical composition) had a considerably broad distribution of values and there was an overlapping of the values obtained for the different types of cement. Five of the 16 cements originally classified as type I cements, but later classified as type II when the maximum of 50 percent for C_3S was deleted, had heat of hydration values greater than the 70 cal/g permitted by specifications for type II cements.

In table 5–2 are presented selected equations computed by the least squares method for both the AE+NAE and the NAE cements. Use of only the major potential compounds as in eqs 1 and 4 resulted in highly significant reductions in the S.D. values. (See table 5–13.) The added effects of other commonly determined variables, K_2O, SO_3, loss and fineness, each of which appeared to have a significant relationship to the heat of hydration, are presented in eqs 2 and 5. The coef./s.d. ratio for C_4AF was less than one when the additional variables were included, with both the AE+NAE and the NAE cements. The additional use of the trace elements, Cu, Cr, Zr, and P as in eqs 3 and 6 resulted in further significant reductions in the S.D. values and in a reduction of the coef./s.d. ratio for C_2S to less than one. (See table 5–13.)

The change of the coefficient or of the coef./s.d. ratio for a compound when added variables are

TABLE 5–1. *Frequency distribution of cements with respect to heat of hydration at 7 days*

Type cement	Heat of hydration, calories per gram												Total
	40 to 45	45 to 50	50 to 55	55 to 60	60 to 65	65 to 70	70 to 75	75 to 80	80 to 85	85 to 90	90 to 95	95 to 100	
	Number of cements												
I				1	2	11	19	19	16	10	2		80
IA						3	1	1	2				7
II*					6	5	3	2					16
IIA*						1							1
II		1		8	21	13	5						48
IIA					1								1
III						1	3	2	6	4	2	1	19
IIIA											1		1
IV and V	1	2	2	6	4								15
Total	1	3	2	15	34	34	31	24	24	14	5	1	188

*Originally classified as type I or IA.

TABLE 5–2. *Coefficients for equations relating the 7-day heat of hydration to various independent variables*

Equation	Type cement	Note	H	C_3A	C_3S	C_2S	C_4AF	K_2O	SO_3	Loss	APF	Cu	Cr	Zr	P	S.D.
1	AE+NAE	(1)	H(7)=	+2.514	+0.822	+0.1880	+0.4751									5.343
			s.d.=	(0.136)	(0.041)	(0.0516)	(0.1880)									
2	do	(1)	HH(7)=	+2.065	+0.634	+0.0862	*+0.1393	+4.945	+3.703	[illegible].523	+0.00403					4.533
			s.d.=	(0.145)	(0.051)	(0.0460)	(0.1685)	(1.805)	(1.330)	[illegible].723)	(0.00093)					
3	do	(1)	HH(7)=	+2.129	+0.570	*+0.029	+0.2103	+5.730	+3.747	−4.170	+0.00476	−75.52	+250.5	+20.55	−7.87	4.260
			s.d.=	(0.139)	(0.051)	(0.045)	(0.1653)	(1.768)	(1.252)	(0.696)	(0.00090)	(40.79)	(79.1)	(8.22)	(3.02)	
3A	do	(2)	HH(7) (odd)=	+2.132	+0.581	*+0.0587	*+0.0596	+8.246	+4.324	−4.217	+0.00392	*+14.22	+189.8	+24.83	−15.36	4.158
			s.d.=	(0.201)	(0.077)	(0.0635)	(0.2381)	(2.561)	(1.916)	(0.947)	(0.00120)	(60.92)	(106.4)	(8.50)	(5.21)	
3B	do	(2)	HH(7) (even)=	+2.192	+0.559	*−0.0006	+0.2804	+3.044	+2.489	−4.383	+0.00626	−130.7	+314.3	*−44.04	−6.77	4.246
			s.d.=	(0.195)	(0.070)	(0.0685)	(0.2414)	(2.515)	(1.739)	(1.094)	(0.00142)	(56.3)	(128.3)	(69.48)	(3.81)	
4	NAE	(3)	HH(7)=	+2.500	+0.828	+0.2006	+0.4325									5.395
			s.d.=	(0.142)	(0.042)	(0.0538)	(0.1933)									
5	do	(3)	HH(7)=	+2.045	+0.639	+0.0968	*+0.0893	+5.307	+3.574	−3.433	+0.00410					4,558
			s.d.=	(0.149)	(0.052)	(0.0477)	(0.1725)	(1.856)	(1.358)	(0.743)	(0.00095)					
6	do	(3)	HH(7)=	+2.109	+0.579	*+0.0410	+0.1760	+6.124	+3.655	−4.142	+0.00477	−82.37	+224.0	+20.97	−8.23	4.280
			s.d.=	(0.143)	(0.052)	(0.0474)	(0.1684)	(1.820)	(1.278)	(0.717)	(0.00091)	(41.09)	(81.5)	(8.30)	(3.05)	
6A	do	(4)	HH(7) (even)=	+1.957	+0.530	*−0.0268	*+0.1238	+8.857	+3.416	+4.697	+0.00642	−67.79	+178.7	*+15.40	−9.14	4.279
			s.d.=	(0.201)	(0.072)	(0.0632)	(0.2760)	(2.549)	(1.856)	(1.099)	(0.00150)	(64.70)	(108.6)	(20.03)	(4.52)	
6B	do	(4)	HH(7) (even)=	+2.338	+0.604	+0.1448	*+0.1470	*+2.010	+3.255	−4.045	+0.00397	−105.30	+297.4	+19.12	−8.56	4.290
			s.d.=	(0.215)	(0.084)	(0.0761)	(0.2231)	(2.682)	(1.903)	(0.994)	(0.00117)	(54.37)	(128.9)	(9.37)	(4.37)	

[1] 172 cements, avg.=71.15, S.D.=9.788. [2] 86 cements. [3] 162 cements, avg.=71.02, S.D.=9.867. [4] 81 cements. *Coef./s.d. ratio less than 1.

TABLE 5–3. *Coefficients for equations relating the 7-day heat of hydration to various independent variables*

Equation	Type cement	Note		Al_2O_3	Fe_2O_3	CaO	SiO_2	K_2O	SO_3	Loss	APF	Cu	Cr	Zr	P	S.D.
1	AE+NAE	(1)	HH(7)=	+1.735	−3.778	+2.761	−4.691									5.139
			s.d.=	(0.588)	(0.517)	(0.205)	(0.491)									
2	do	(1)	HH(7)=	+1.659	−3.880	+2.316	−4.079	+4.935	+2.072	−3.512	+0.00403					4.534
			s.d.=	(0.597)	(0.457)	(0.221)	(0.484)	(1.806)	(1.329)	(0.723)	(0.00093)					
3	do	(1)	HH(7)=	+1.970	−3.743	+2.231	−4.085	+5.710	+2.174	−4.158	+0.00476	−76.40	+250.2	+20.41	−7.93	4.260
			s.d.=	(0.566)	(0.456)	(0.212)	(0.459)	(1.770)	(1.251)	(0.696)	(0.00090)	(40.80)	(79.1)	(8.22)	(3.02)	
3A	do	(2)	HH(7) (odd)=	+2.053	−4.193	+2.184	−3.913	+8.213	+2.798	−4.200	+0.00392	*−13.59	+192.1	+24.73	−15.28	4.163
			s.d.=	(0.805)	(0.676)	(0.284)	(0.591)	(2.567)	(1.911)	(0.948)	(0.00120)	(61.00)	(106.5)	(8.51)	(5.21)	
3B	do	(2)	HH(7) (even)=	+2.060	−3.647	+2.280	−4.259	+3.032	*+0.877	−4.383	+0.00625	−132.2	+312.2	*−45.42	−6.93	4.244
			s.d.=	(0.819)	(0.650)	(0.330)	(0.739)	(2.515)	(1.752)	(1.094)	(0.00142)	(56.4)	(128.2)	(69.44)	(3.81)	
4	NAE	(3)	HH(7)=	+1.741	−3.883	+2.748	−4.634									5.184
			s.d.=	(0.614)	(0.531)	(0.213)	(0.511)									
5	do	(3)	HH(7)=	+1.637	−3.995	+2.300	−4.020	+5.294	+1.948	−3.418	+0.00410					4.558
			s.d.=	(0.617)	(0.468)	(0.228)	(0.500)	(1.856)	(1.357)	(0.743)	(0.00095)					
6	do	(3)	HH(7)=	+1.921	−3.814	+2.231	−4.049	+6.098	+2.074	−4.125	+0.00477	−83.38	+223.2	+20.82	−8.30	4.277
			s.d.=	(0.583)	(0.465)	(0.217)	(0.473)	(1.820)	(1.277)	(0.716)	(0.00091)	(41.08)	(81.4)	(8.30)	(3.05)	
6A	do	(4)	HH(7) (odd)=	+1.516	−3.710	+2.236	−4.256	+8.845	*+1.827	−4.674	+0.00641	−69.01	+180.4	*+15.43	−9.11	4.274
			s.d.=	(0.769)	(0.770)	(0.280)	(0.601)	(2.548)	(1.838)	(1.098)	(0.00150)	(64.62)	(108.4)	(20.00)	(4.52)	
6B	do	(4)	HH(7) (even)=	+2.887	−4.217	+2.015	−3.344	*+1.956	*+1.809	−4.031	+0.00396	−106.20	+292.7	+18.87	−8.72	4.290
			s.d.=	(0.965)	(0.611)	(0.367)	(0.804)	(2.684)	(1.935)	(0.994)	(0.00117)	(54.39)	(128.9)	(9.37)	(4.37)	

[1] 172 cements, avg.=71.15, S.D.=9.788. [2] 86 cements. [3] 162 cements, avg.=71.02, S.D.=9.867. [4] 81 cements. *Coef./s.d. ratio less than 1.

Table 5–4. *Calculated contribution of independent variables to the 7-day heat of hydration*

Independent variable	Range of variable	Coefficients from equation 6, table 5–2	Calculated contribution to HH(7)	Calculated range of contribution to HH(7)
C_3A	0 to 15 %	+2.10	0 to +31.5	31.5
C_3S	30 to 70 %	+0.58	+17.4 to +40.6	23.2
C_2S	5 to 50 %	+0.04	+0.2 to +2.0	1.8
C_4AF	4 to 17 %	+0.18	+0.7 to +3.1	2.4
K_2O	0 to 1.1 %	+6.1	0 to +6.7	6.7
SO_3	1.2 to 3.6 %	+3.7	+4.4 to +13.3	8.8
Loss	0.3 to 3.6 %	−4.1	−1.2 to −14.8	13.6
APF (cm^2/g)	2500 to 5500	+0.0048	+12.0 to +26.4	14.4
Cu	0 to 0.05%	−82	0 to −4.1	4.1
Cr	0 to 0.02%	+224	0 to +4.5	4.5
Zr	0 to 0.5 %	+21	0 to +10.5	10.5
P	0 to 0.5 %	−8	0 to −4.0	4.0

included, does not, of course, mean that the actual contribution of the compound to the heat of hydration has changed, but that the information about that contribution has changed. For example, eq 4, table 5–2, with only the four compounds results in a pretty good prediction of the heat of hydration, but in eq 5 the prediction due to eight variables is even better, as shown by the reduced S.D., and C_4AF is here taking an ineffectual part in the prediction in conjunction with the other seven variables. In eq 6 the ability to predict is still better with both C_2S and C_4AF giving a negligible contribution.

Using the same variables as were used for all the cements in eqs 3 and 6, the equations for the "odds" and "evens" in the array of cements resulted in the relationships 3A and 3B for the AE+NAE cements and 6A and 6B for the NAE cements. The C_2S, C_4AF, K_2O, Cu, and Zr had coef./s.d. ratios less than 1 in either the "odds" or "evens" or both. As indicated in previous sections, this may occur when the coef./s.d. ratio is not significant in the equation for all the values, or when a preponderance of the cements with very high or very low values for an independent variable happens to fall within one of the groups.

In table 5–3 are presented a similar series of equations using the oxides present in major quantities instead of the potential compound compositions. The S.D. values obtained in this series of equations do not differ appreciably from those presented in table 5–2. The use of the major oxides in eqs 1 and 4, resulted in highly significant reduction in the S.D. values. As in table 5–2 the use of other commonly determined variables resulted in a further significant reduction, and the use of the minor constituent resulted in a still further reduction in the S.D. values. The coefficients of the major oxides, table 5–3, were not affected to so great an extent as were those of the C_2S and C_4AF in table 5–2 by the addition of other variables. In table 5–3 eqs 3A and 3B, or 6A and 6B, for the "odds" and "evens" instances occurred where the K_2O, SO_3, Cu, and Zr had coef./s.d. ratios of less than 1.

Table 5–5. *Frequency distribution of cements with respect to heat of hydration at 28 days*

Type cement	Heat of hydration, calories per gram												Total
	50 to 55	55 to 60	60 to 65	65 to 70	70 to 75	75 to 80	80 to 85	85 to 90	90 to 95	95 to 100	100 to 105	105 to 110	
	Number of cements												
I	----	----	----	----	----	6	17	23	23	5	5	1	80
IA	----	----	----	----	----	1	3	----	3	----	----	----	7
II*	----	----	----	2	3	4	3	2	2	----	----	----	16
IIA*	----	----	----	----	----	----	1	----	----	----	----	----	1
II	----	----	----	2	13	14	16	3	----	----	----	----	48
IIA	----	----	----	----	----	----	1	----	----	----	----	----	1
III	----	----	----	----	----	2	3	3	4	3	1	3	19
IIIA	----	----	----	----	----	----	----	----	----	1	----	----	1
IV & V	1	----	1	7	3	3	----	----	----	----	----	----	15
Total	1	----	1	11	19	30	44	31	32	9	6	4	188

*Originally classified as type I or IA.

In table 5–4 are presented the calculated contributions and ranges of contributions to the 7-day heat of hydration. The coefficients of the independent variables of equation 6, table 5–2 were used together with the approximate range of the values for the different variables for the cements used in this study. K_2O and SO_3 content and fineness appear to have had an appreciable effect on the 7-day heat of hydration. There is also an indication that an increase in Cu, P, or loss on ignition was accompanied by lower heat of hydration values, whereas an increase in Cr or Zr content may be associated with an increase in the heat of hydration.

4.3. Heat of Hydration at 28 Days

The frequency distribution of the 28-day heat of hydration values obtained on the cements of the different types is presented in table 5–5. The distribution of values with respect to the different types was similar to that obtained at 7 days and presented in table 5–1.

In table 5–6 are presented selected equations relating the 28-day heat of hydration to various independent variables. The use of the four major potential compounds, as in eqs 1 and 4 resulted in a highly significant reduction in the S.D. value. The use of loss on ignition and fineness in eqs 2 and 5 reduced the S.D. further, and a further significant reduction was attained by the use of the minor constituents SrO, Cu, Co, Zr, and P as noted in eqs 3 and 6. (See also table 5–13.) In preliminary trial equations the SO_3, K_2O and Cr, which had an effect at 7 days, were found to have no significant effect on the 28-day heat of hydration. The equations computed for the "odds" and "evens", equations 3A and 3B or 6A and 6B, indicated that the relationships of Cu, Co, and Zr with 28-day heat of hydration may be questionable.

In table 5–7 are presented a similar series of equations using the major oxides instead of the potential compounds. The S.D. values in table 5–7 are comparable to those in table 5–6 and again

TABLE 5–6. *Coefficients for equations relating the 28-day heat of hydration to various independent variables*

Equation	Type cement	Note		C3A	C3S	C2S	C4AF	Loss	APF	SrO	Cu	Co	Zr	P	S.D.
1	AE+NAE	[1]	HH(28)=	+2.593	+0.9165	+0.3302	+0.8503								4.802
			s.d.=	(0.122)	(0.0365)	(0.0464)	(0.1690)								
2	do	[1]	HH(28)=	+2.573	+0.7962	+0.2727	+0.7888	−2.167	+0.00311						4.599
			s.d.=	(0.118)	(0.0514)	(0.0467)	(0.1636)	(0.728)	(0.00080)						
3	do	[1]	HH(28)=	+2.781	+0.7845	+0.2526	+1.0503	−2.996	+0.00327	−10.91	−141.0	−423.1	+15.5	−8.24	4.206
			s.d.=	(0.131)	(0.0484)	(0.0435)	(0.1573)	(0.689)	(0.00073)	(4.16)	(40.7)	(243.8)	(8.2)	(3.06)	
3A	do	[2]	HH(28)(odd)=	+2.999	+0.7685	+0.2486	+1.1421	−3.762	+0.00294	−14.67	*−58.7	−1166.2	+18.9	−13.97	4.263
			s.d.=	(0.193)	(0.0723)	(0.0602)	(0.2278)	(0.961)	(0.00105)	(5.88)	(73.2)	(485.6)	(8.8)	(5.33)	
3B	do	[2]	HH(28)(even)=	+2.588	+0.7853	+0.2310	+0.9143	−2.392	+0.00393	−7.28	−135.6	−227.8	*+47.5	−6.70	4.165
			s.d.=	(0.192)	(0.0693)	(0.0671)	(0.2335)	(1.060)	(0.00113)	(6.10)	(54.3)	(293.4)	(64.8)	(3.91)	
4	NAE	[3]	HH(28)=	+2.601	+0.9139	+0.3280	+0.8641								4.883
			s.d.=	(0.129)	(0.0379)	(0.0487)	(0.1749)								
5	do	[3]	HH(28)=	+2.575	+0.7946	+0.2693	+0.8009	−2.117	+0.00311						4.679
			s.d.=	(0.124)	(0.0531)	(0.0490)	(0.1695)	(0.757)	(0.00082)						
6	do	[3]	HH(28)=	+2.791	+0.7872	+0.2563	+1.0668	−3.016	+0.00322	−12.37	−143.8	−503.4	+15.58	−8.14	4.237
			s.d.=	(0.133)	(0.0493)	(0.0451)	(0.1608)	(0.713)	(0.00076)	(4.42)	(41.3)	(254.2)	(8.31)	(3.10)	
6A	do	[4]	HH(28)(odd)=	+2.850	+0.7083	+0.2035	+1.0977	−3.607	+0.00459	−12.83	−133.3	−643.3	*+21.04	−7.83	4.554
			s.d.=	(0.213)	(0.0728)	(0.0658)	(0.2779)	(1.222)	(0.00133)	(7.07)	(73.4)	(381.5)	(22.15)	(4.87)	
6B	do	[4]	HH(28)(even)=	+2.668	+0.8823	+0.3022	+0.9471	−2.934	+0.00216	−11.10	−146.5	*−308.0	+13.20	−8.05	4.078
			s.d.=	(0.191)	(0.0758)	(0.0671)	(0.2114)	(0.919)	(0.00099)	(6.24)	(50.8)	(378.2)	(8.84)	(4.36)	

[1] 172 cements, avg.=83.62, S.D.= 8.997. [2] 86 cements. [3] 162 cements, avg.=83.49, S.D.=9.125. [4] 81 cements. *Coef./s.d. ratio less than 1.

TABLE 5–7. *Coefficients for equations relating the 28-day heat of hydration to various independent variables*

Equation	Type cements	Note		Al_2O_3	Fe_2O_3	CaO	SiO_2	Loss	APF	SrO	Cu	Co	Zr	P	S.D.
1	AE+NAE	[1]	HH(28)=	+2.260	−2.748	+2.616	−3.967								4.783
			s.d.=	(0.547)	(0.481)	(0.191)	(0.457)								
2	do	[1]	HH(28)=	+2.656	−2.785	+2.390	−3.674	−2.263	+0.00257						4.627
			s.d.=	(0.563)	(0.466)	(0.226)	(0.492)	(0.733)	(0.00083)						
3	do	[1]	HH(28)=	+3.225	−2.362	+2.411	−3.799	−3.135	+0.00272	−11.95	−135.7	−457.1	+16.83	−8.20	4.220
			s.d.=	(0.557)	(0.450)	(0.210)	(0.457)	(0.692)	(0.00078)	(4.17)	(40.9)	(245.1)	(8.21)	(3.07)	
3A	do	[2]	HH(28) (odd)=	+3.842	−2.526	+2.392	−3.774	−4.026	+0.00251	−16.55	*−54.2	−1168.0	+20.90	−13.51	4.259
			s.d.=	(0.767)	(0.681)	(0.287)	(0.606)	(0.961)	(0.00108)	(5.89)	(73.2)	(485.1)	(8.75)	(5.32)	
3B	do	[2]	HH(28) (even)=	+2.662	−2.357	+2.443	−3.870	−2.316	+0.00312	−7.68	−135.2	*−290.3	*+51.16	−6.77	4.206
			s.d.=	(0.874)	(0.639)	(0.330)	(0.733)	(1.070)	(0.00119)	(6.15)	(55.0)	(297.3)	(65.41)	(3.95)	
4	NAE	[3]	HH(28)=	+2.302	−2.727	+2.615	−3.974								4.857
			s.d.=	(0.575)	(0.498)	(0.199)	(0.479)								
5	do	[3]	HH(28)=	+2.666	−2.759	+2.394	−3.693	−2.212	+0.00256						4.704
			s.d.=	(0.592)	(0.482)	(0.235)	(0.514)	(0.762)	(0.00085)						
6	do	[3]	HH(28)=	+3.254	−2.330	+2.413	−3.772	−3.158	+0.00267	−13.38	−139.1	−535.4	+16.96	−8.13	4.244
			s.d.=	(0.572)	(0.459)	(0.215)	(0.470)	(0.714)	(0.00079)	(4.43)	(41.5)	(255.1)	(8.32)	(3.11)	
6A	do	[4]	HH(28) (odd)=	+3.591	−2.359	+2.327	−3.757	−3.792	+0.00378	−14.79	−117.1	−753.1	+25.74	−7.99	4.504
			s.d.=	(0.791)	(0.808)	(0.302)	(0.651)	(1.207)	(0.00135)	(7.02)	(73.0)	(380.1)	(21.93)	(4.81)	
6B	do	[4]	HH(28) (even)=	+2.772	−2.544	+2.548	−3.898	−3.006	+0.00188	−12.28	−147.9	*−285.3	+14.51	−7.99	4.168
			s.d.=	(0.939)	(0.601)	(0.354)	(0.780)	(0.941)	(0.00104)	(6.35)	(52.0)	(386.4)	(9.02)	(4.46)	

[1] 172 cements, avg.=83.62, S.D.=8.997. [2] 86 cements. [3] 162 cements, avg.=83.49, S.D.=9.125. [4] 81 cements. *Coef./s.d. ratio less than 1.

Table 5-8. *Calculated contributions of independent variables to the 28-day heat of hydration*

Independent variable	Range of variable	Coefficients from equation 6, table 5-6	Calculated contribution to HH(28)	Calculated range of contribution to HH(28)
C_3A	0 to 15 %	+2.8	0 to +42.0	42.0
C_3S	30 to 70 %	+0.79	+23.7 to +55.3	31.6
C_2S	5 to 50 %	+0.26	+1.3 to +13.0	11.7
C_4AF	4 to 17 %	+1.07	+4.3 to +18.2	13.9
Loss	0.3 to 3.6 %	−3.02	−0.9 to −10.9	10.0
APF (cm^2/g)	2500 to 5500	+0.0032	+8.0 to +17.6	9.6
SrO	0 to 0.4 %	−12.4	0 to −5.0	5.0
Cu	0 to 0.05%	−143	0 to −7.2	7.2
Co	0 to 0.01%	−503	0 to −5.0	5.0
Zr	0 to 0.5 %	+15.6	0 to +7.8	7.8
P	0 to 0.5 %	−8.1	0 to −4.0	4.0

Table 5-9. *Frequency distribution of cements with respect to 1-year heat of hydration*

Type cement	Heat of hydration, calories per gram								Total
	80 to 85	85 to 90	90 to 95	95 to 100	100 to 105	105 to 110	110 to 115	115 to 120	
	Number of cements								
I		2	5	17	25	12		2	63
IA			3	1	1	2			7
II*		2	3	5	2				12
IIA*				1					1
II		10	17	8					35
IIA			1						1
III				3	3	3	5		14
IIIA							1		1
IV & V	1	3	2						6
Total	1	17	31	35	31	17	6	2	140

*Originally classified as type I or IA.

indicate the effect of loss on ignition and fineness as well as the trace elements. (See also table 5-13.)

The calculated contributions to the 28-day heat of hydration together with the calculated ranges of such contributions are presented in table 5-8. It may be noted that the effects of C_2S and C_4AF are greater than they were at 7 days. This also appears to be the case with loss on ignition and Cu whereas the opposite may be noted for the effect of fineness and Zr.

4.4. Heat of Hydration at 1 Year

The frequency distributions of the 1-year heat of hydration values are presented in table 5-9. The distributions for the different types of cement overlapped to a greater extent than was noted for the 7- and 28-day heat of hydration values.

In table 5-10 are presented the computed equations relating the heat of hydration at 1 year to various independent variables.

By using only the major potential compounds as in eqs 1 and 4 of table 5-10, there was a significant reduction in the S.D. values. When such other ordinarily determined values as Na_2O, loss on ignition, and fineness were included (eqs 2 and 5) the S.D. values showed a further significant reduction. It may also be noted that by using the trace elements Cu, V, Ba, and P in the computed

Table 5-10. *Coefficients for equations relating the 1-year heat of hydration to various independent variables*

Equation	Type cement	Note		C_3A	C_3S	C_2S	C_4AF	Na_2O	Loss	APF	Cu	V	Ba	P	S.D.
1	AE+NAE	[1]	HH(1Y) =	+2.334	+1.135	+0.6086	+0.6914								3.963
			s.d. =	(0.117)	(0.035)	(0.0478)	(0.1663)								
2	do	[1]	HH(1Y) =	+2.333	+1.033	+0.5969	+0.6415	−5.092	−2.185	+0.00278					3.645
			s.d. =	(0.116)	(0.047)	(0.0457)	(0.1585)	(1.912)	(0.670)	(0.00075)					
3	do	[1]	HH(1Y) =	+2.388	+1.044	+0.5746	+0.7935	−5.262	−2.323	+0.00266	−111.2	+46.93	−36.36	−7.26	3.418
			s.d. =	(0.122)	(0.046)	(0.0462)	(0.1563)	(1.802)	(0.637)	(0.00071)	(39.9)	(21.78)	(14.70)	(2.62)	
3A	do	[2]	HH(1Y)(odd) =	+2.232	+1.008	+0.6518	+0.6622	−5.261	−1.357	+0.00311	−183.8	+32.20	−37.25	−6.84	3.349
			s.d. =	(0.173)	(0.071)	(0.0644)	(0.2058)	(2.174)	(0.903)	(0.00103)	(62.1)	(25.03)	(17.56)	(3.68)	
3B	do	[2]	HH(1Y)(even) =	+2.462	+1.062	+0.5011	+0.7211	−6.243	−2.919	+0.00291	*−36.72	+88.09	*−13.29	−7.63	3.516
			s.d. =	(0.187)	(0.065)	(0.0724)	(0.2899)	(3.565)	(0.964)	(0.00110)	(63.64)	(51.06)	(34.02)	(4.07)	
4	NAE	[3]	HH(1Y) =	+2.290	+1.140	+0.6239	+0.6622								3.987
			s.d. =	(0.123)	(0.036)	(0.0504)	(0.1722)								
5	do	[3]	HH(1Y) =	+2.277	+1.047	+0.6164	+0.6056	−5.264	−2.400	+0.00277					3.630
			s.d. =	(0.119)	(0.048)	(0.0479)	(0.1624)	(1.946)	(0.691)	(0.00076)					
6	do	[3]	HH(1Y) =	+2.333	+1.060	+0.5993	+0.7592	−5.331	−2.553	+0.00262	−118.6	+43.23	−36.90	−7.22	3.371
			s.d. =	(0.125)	(0.046)	(0.0480)	(0.1584)	(1.817)	(0.649)	(0.00071)	(39.7)	(21.84)	(14.72)	(2.61)	
6A	do	[4]	HH(1Y)(odd) =	+2.228	+1.006	+0.6162	+0.7475	−5.306	−2.232	+0.00377	−231.9	*+18.96	−54.75	−9.24	2.986
			s.d. =	(0.175)	(0.056)	(0.0596)	(0.2264)	(1.975)	(0.868)	(0.00098)	(60.1)	(26.44)	(19.17)	(3.72)	
6B	do	[4]	HH(1Y)(even) =	+2.386	+1.136	+0.6133	+0.7313	−6.061	−2.799	+0.00133	*−51.97	+51.25	−33.80	−5.99	3.689
			s.d. =	(0.195)	(0.082)	(0.0820)	(0.2380)	(3.753)	(0.973)	(0.00111)	(59.97)	(38.22)	(24.43)	(3.90)	

[1] 127 cements, avg.=98.09, S.D.=7.031. [2] 63 or 64 cements. [3] 117 cements, avg.=98.00, S.D.=7.049. [4] 58 or 59 cements. *Coef./s.d. ratio less than 1.

TABLE 5-11. *Coefficients for equations relating the 1-year heat of hydration to various independent variables*

Equation	Type cement	Note		Al_2O_3	Fe_2O_3	CaO	SiO_2	Na_2O	Loss	APF	Cu	V	Ba	P	S.D.
1	AE+NAE	[1]	HH(1Y) = s.d. =	+1.463 (0.486)	−2.809 (0.456)	+2.658 (0.176)	−3.247 (0.431)								3.877
2	do	[1]	HH(1Y) = s.d. =	+2.032 (0.489)	−2.804 (0.425)	+2.384 (0.213)	−2.745 (0.473)	−5.132 (1.895)	−2.244 (0.665)	+0.00217 (0.00077)					3.615
3	do	[1]	HH(1Y) = s.d. =	+1.972 (0.476)	−2.487 (0.431)	+2.480 (0.204)	−2.970 (0.457)	−5.337 (1.795)	−2.372 (0.635)	+0.00203 (0.00074)	−103.8 (39.8)	+41.4 (21.7)	−37.6 (14.6)	−6.95 (2.61)	3.404
3A	do	[2]	HH(1Y)(odd) = s.d. =	+2.105 (0.639)	−2.480 (0.547)	+2.153 (0.281)	−2.152 (0.607)	−5.525 (2.107)	−1.530 (0.879)	+0.00257 (0.00103)	−177.0 (60.1)	+27.3 (24.1)	−40.0 (17.0)	−6.79 (3.57)	3.245
3B	do	[2]	HH(1Y)(even) = s.d. =	+1.776 (0.780)	−3.025 (0.811)	+2.708 (0.333)	−3.559 (0.760)	−6.320 (3.662)	−2.778 (0.989)	+0.00215 (0.00118)	*−24.4 (65.4)	+88.1 (52.5)	*−8.2 (34.8)	−6.80 (4.14)	3.611
4	NAE	[3]	HH(1Y) = s.d. =	+1.403 (0.508)	−2.820 (0.470)	+2.637 (0.184)	−3.168 (0.452)								3.900
5	do	[3]	HH(1Y) = s.d. =	+1.899 (0.505)	−2.187 (0.435)	+2.382 (0.218)	−2.689 (0.489)	−5.250 (1.930)	−2.456 (0.686)	+0.00215 (0.00078)					3.602
6	do	[3]	HH(1Y) = s.d. =	+1.861 (0.485)	−2.493 (0.434)	+2.468 (0.207)	−2.879 (0.468)	−5.360 +1.809	−2.602 (0.647)	+0.00200 (0.00074)	−111.9 (39.5)	+37.88 (21.72)	−38.9 (21.7)	−6.95 (2.59)	3.356
6A	do	[4]	HH(1Y)(odd) = s.d. =	+2.085 (0.578)	−2.153 (0.583)	+2.180 (0.245)	−2.277 (0.555)	−5.420 (1.992)	−2.262 (0.876)	+0.00308 (0.00103)	−227.0 (60.8)	*+12.39 (26.56)	−51.5 (19.3)	−8.53 (3.74)	3.012
6B	do	[4]	HH(1Y)(even) = s.d. =	+1.590 (0.939)	−2.890 (0.693)	+2.734 (0.392)	−3.356 (0.882)	−6.083 (3.748)	−2.806 (0.971)	*+0.00083 (0.00115)	*−40.6 (59.8)	+51.21 (38.16)	−40.1 (24.4)	−6.30 (3.90)	3.680

[1] 127 cements, avg.=98.09, S.D.=7.031. [2] 63 or 64 cements. [3] 117 cements, avg.=98.00, S.D.=7.049. [4] 58 or 59 cements. *Coef./s.d. ratio less than 1.

TABLE 5-12. *Calculated contributions of independent variables to the 1-year heat of hydration*

Independent variable	Range of variable	Coefficients from equation 6, table 5-10	Calculated contribution to HH(1Y)	Calculated range of contribution to HH(1Y)
C_3A	0 to 15 %	+2.33	0 to +34.9	34.9
C_3S	30 to 70 %	+1.06	+32.8 to +74.2	42.4
C_2S	5 to 50 %	+0.60	+3.0 to +30.0	27.0
C_4AF	4 to 17 %	+0.76	+3.0 to +12.9	9.9
Na_2O	0 to 0.75%	−5.33	0 to −4.0	4.0
Loss	0.3 to 3.6 %	−2.55	−0.8 to −9.2	8.4
APF (cm^2/g)	2500 to 5500	+0.0026	+6.5 to +14.3	7.8
Cu	0 to 0.05%	−119	0 to −5.9	5.9
V	0 to 0.1 %	+43	0 to +4.3	4.3
Ba	0 to 0.2 %	−37	0 to −7.4	7.4
P	0 to 0.5 %	−7.2	0 to −3.6	3.6

TABLE 5-13. *"F" values for significance of reduction of variance due to added variables.*

Table	Equations	"F" ratio	D.F.	Critical F $\alpha=0.01$	Critical F $\alpha=0.05$
5-2	*0, 1 1, 2 2, 3	102.3 17.4 6.4	4:168 4:164 4:160	3.45 3.45 3.45	2.45 2.45 2.45
5-2	**0, 4 4, 5 5, 6	96.0 16.8 6.2	4:158 4:154 4:150	3.45 3.45 3.45	2.45 2.45 2.45
5-3	*0, 1 1, 2 2, 3	114.0 13.0 6.4	4:168 4:164 4:160	3.45 3.45 3.45	2.45 2.45 2.45
5-3	**0, 4 4, 5 5, 6	107.2 12.6 6.2	4:158 4:154 4:150	3.45 3.45 3.45	2.45 2.45 2.45
5-6	*0, 1 1, 2 2, 3	108.9 8.6 7.5	4:168 2:166 5:161	3.45 4.75 3.13	2.45 3.05 2.28
5-6	**0, 4 4, 5 5, 6	101.9 8.0 7.8	4:158 2:156 5:151	3.45 4.75 3.12	2.45 3.05 2.28
5-7	*0, 1 1, 2 2, 3	110.0 6.8 7.7	4:168 2:166 5:161	3.45 4.75 3.15	2.45 3.05 2.28
5-7	**0, 4 4, 5 5, 6	103.4 6.2 8.1	4:158 2:156 5:151	3.45 4.75 3.15	2.45 3.05 2.28
5-10	*0, 1 1, 2 2, 3	69.2 8.5 5.1	4:123 3:120 4:116	3.50 3.95 3.50	2.45 2.68 2.45
5-10	**0, 4 4, 5 5, 6	63.2 8.8 5.4	4:113 3:110 4:106	3.50 3.97 3.50	2.45 2.69 2.45
5-11	*0, 1 1, 2 2, 3	73.7 7.2 4.8	4:123 3:120 4:116	3.50 3.95 3.50	2.45 2.68 2.45
5-11	**0, 4 4, 5 5, 6	67.3 7.5 5.2	4:113 3:110 4:106	3.50 3.97 3.50	2.45 2.70 2.45

*AE+NAE cements. **NAE cements.

eqs 3 and 6 a further significant reduction in S.D. values was attained.

The equations for the "odds" and "evens" in the array of cements indicated that Cu, V, and Ba had coef./s.d. ratios less than one in some instances.

By use of the principal oxides as in table 5-11 instead of the potential compounds as in the previous table similar results were obtained. The use of only the principal oxides (eqs 1 and 4) resulted in highly significant reductions in the S.D. values. As also presented in the previous table, the use of Na_2O, loss on ignition, and fineness (eqs 2 and 5) or these variables with the addition of the trace elements Cu, V, Ba, and P (eqs 3 and 6) each resulted in significantly lower S.D. values.

For the equations computed for the "odds" and "evens" (3A, 3B, 6A, and 6B) there were instances when the Cu, V, Ba, as well as fineness had coef./s.d. values less than one.

In table 5–12 are presented the calculated contributions of the various independent variables to the 1-year heat of hydration as well as the calculated ranges of contributions for the different variables.

5. Discussion

5.1. Age of Test Versus Trace Element Effect

The minor and trace elements which apparently had effects on heat of hydration were not always the same for the different ages. Some were significant at some ages but not at others, and the coef./s.d. ratios of some were different at different ages (see tables 5–2, 5–6 and 5–10; also 5–3, 5–7 and 5–11). Reference will be made specifically to the equations for the NAE cements in these tables. The loss on ignition, air permeability fineness, and P were highly significant at all ages and were consistent with published information relative to their effects. In the equations for the relationship between 7-day heat of hydration and major compounds, the coef./s.d. ratios for K_2O, SO_3, Cr, Cu, and Zr were also highly significant. Where the major oxides were used in the equations this was also true except for the SO_3 which was of questionable significance. In the equations for the 28-day heat of hydration both with compounds and with oxides, the coef./s.d. ratios for K_2O, SO_3, and Cr were less than one and therefore do not appear. The ratios for SrO and Cu were significant at the one percent level and that of Co at the five percent level. The significance of Zr was less at 28 days than at 7 days, whereas the ratio for Cu became more significant. In both sets of equations for the one year heat of hydration the coefficient for Na_2O was highly significant and had a negative value, whereas K_2O which was the significant alkali and had a positive coefficient at 7 days, was not significant. The coef./s.d. ratios for SrO, Co, Cr and Zr were all less than one in preliminary equations and therefore do not appear in the tables. V and Ba appeared significant in the 1-year equations with the potential compounds and less significant when the calculations were made with the major oxides.

5.2. Effect of Minor Constituents and Trace Elements on Calculated Coefficients of the Major Calculated Compounds

Data from different sources showing calculated coefficients for the effects of the major potential compounds on heats of hydration at different ages are plotted in figure 5–2. The plotted points at the midpoints of the vertical bars represent the calculated contribution of the compounds to the heat of hydration in terms of calories per gram, and the ends of the bars represent the 95-percent confidence limits.[4] Bars (1), (2), (5), (6), (9), and (10) in each part of figure 5–2 represent data from this investigation taken, respectively, from equations (4) and (6) in tables 5–2, 5–6, and 5–10.

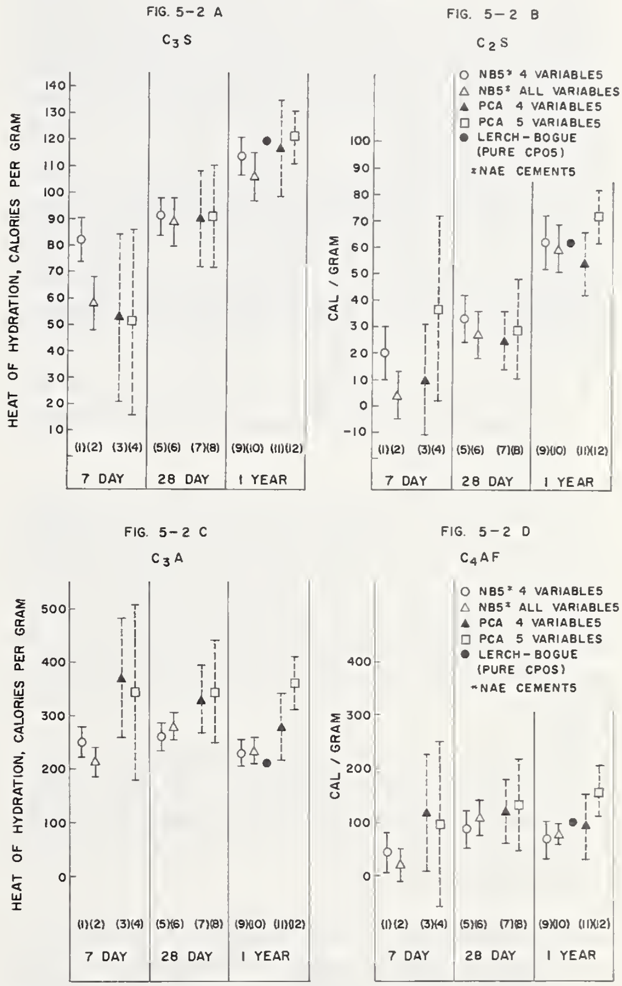

Figure 5–2A, B, C, and D. *Heat of hydration in calories per gram at 7 days, 28 days, and 1 year for C_3S, C_2S, C_3A, and C_4AF.*

[4] The 95-percent confidence limits represent limits computed from the data such that 95-percent of limits so computed (from sets of similar data) will bracket the true value of the coefficient. See, e.g., M. G. Natrella, Experimental Statistics, NBS Handbook 91, pp. 1–11 to 1–13 (1963), U.S. Government Printing Office.

The other bars are taken from other published data and will be discussed further in a later subsection.

In this and subsequent subsections based on figure 5–2, the following statistical criteria will be followed: (1) A *highly significant difference* between two coefficients (whether these represent different ages of test or the same age with and without additional variables) is indicated if the 95-percent confidence limits of the two coefficients do not overlap; (2) a *probable difference* between coefficients is indicated if they differ by more than three times the standard deviation (s.d.), provided that the two s.d.'s are approximately equal; (3) *no difference* between coefficients is demonstrated if one of the two coefficients lies within the 95-percent confidence interval for the other coefficient, unless there is other evidence supporting the assumption of a difference.

Bars (1), (5), and (9) in figure 5–2 represent equation (4) in the three tables in which only the four major compounds were used as independent variables, while bars (2), (6), and (10) represent equation (6) in which a number of other variables were also included.

At the age of 7 days a highly significant reduction in the coefficient for C_3S was caused by inclusion of the additional variables, and a probably significant reduction occurred for C_2S and C_3A. At the other two ages for these three variables and at all ages for C_4AF, no significant difference was indicated.

5.3. Numerical Values of Coefficients of the Major Potential Compounds at Different Ages of Test

Comparing the coefficients obtained at the different ages, bars (2), (6), and (10) in each of figures 5–2 A, B, C, and D, the coefficient increased significantly with age of test for both C_3S and C_2S. The increase was highly significant for all but the 28-day to 1-year increase for C_3S, but even in this case the overlap between confidence intervals was quite small, and the evidence for an increase is strong.

For C_3A and C_4AF a highly significant increase occurred between 7 and 28 days. Between 28 days and 1 year, however, there was a probably significant decrease for C_3A and no evidence of a significant change for C_4AF.

5.4. Comparison of Coefficients of Major Potential Compounds Obtained in this Investigation With Previously Reported Values

Also presented in figure 5–2, parts A, B, C, and D are coefficients relating to heat of hydration reported by Verbeck and Foster [10] of cements of the Portland Cement Association (PCA) long time study of cement performance. The values used in this comparison are those reported for the 12 cements hydrated at 70 ° F and for which least squares computations were made using only the four major compounds (bars (3), (7), and (11) in figure 5–2) and the four major compounds plus SO_3 (bars (4), (8), and (12) in figure 5–2). The PCA data was presented in the original paper together with plus or minus values to indicate probable errors which would correspond to approximately a 48-percent confidence level for the number of tests involved. These values were recomputed in terms of the 95-percent confidence level taking into account the number of degrees of freedom. (The values were verified by recalculating the PCA values by means of the computer.) The lengths of the bars (3), (4), (7), (8), (11), and (12) in figure 5–2 represent the recalculated 95-percent confidence limits for the PCA data with and without SO_3 as a variable.

In general, comparisons between coefficients in the PCA studies and in the present investigation were difficult because of the wide confidence intervals of the former resulting from the small number of tests. There were significant differences, however.

For comparisons of coefficients in equations involving only the four major compounds (bars (1) and (3), (5) and (7), and (9) and (11)) the confidence intervals overlapped in all 12 cases. There were only two cases where the evidence indicated a possible difference, viz, C_3A at 7 and 28 days. In these two cases the coefficient for the NBS data appeared to be lower, indicating a lesser effect for this variable than was found in the PCA data.

With SO_3 as an added variable with the PCA data and a larger number of added variables in the NBS data, highly significant differences were indicated at the age of 1 year for C_3A and C_4AF and probably significant differences at the same age for C_3S and C_2S. The coefficient obtained with the NBS data was lower in each case. For the other two ages, no difference in coefficient between the two studies was detected.

In addition to the wide confidence limits of the PCA data caused by the small number of cements tested, some other factors need to be taken into consideration in comparing the two sets of data. The PCA values included only cements with 1.0 percent or less ignition loss which was not the case with the NBS values. There were also slight differences in test methods and basis of reporting (ignited versus unignited weight of cement) which may have resulted in some differences in the reported values.

Woods, Steinour, and Starke [8] have also given coefficients for regression equations using the four potential compounds and the four principal oxides calculated on the results obtained from 13 laboratory prepared cements. The pastes were stored at 35 ° C (95 ° F) during the hydration period as compared to 23 ° C (73 ° F) required at present. Their equations for 25-day results are as follows:

$$HH(28) = 2.02\ C_3A + 1.14\ C_3S + 0.44\ C_2S + 0.48\ C_4AF$$
$$\text{s.d.} = (0.30)\quad (0.081)\quad (0.067)\quad (0.28)$$
$$\text{S.D.} = 3.80$$

$$HH(28) = 3.31\ CaO - 4.93\ SiO - 3.1\ Fe_2O_3 - 0.1\ Al_2O_3$$

These may be compared, respectively, to eqs 4 in tables 5–6 and 5–7. Agreement is quite good except for Al_2O_3 and C_4AF. The s.d.'s and S.D. were calculated from probable errors given by the authors. They did not report the probable errors for the second equation with the oxides.

Woods et al., also reported on the relationship between heat of hydration at various ages and the function, % C_3S + 2.1 × % C_3A. This simple function, which was calculated on the assumption that the contributions of C_2S and C_4AF were small and equal, was claimed to be "a useful one for quick rough approximation of the *relative* standing of two cements differing only in composition" (italics ours). The author recognized that the application of the results of their analysis to commercial cements should not be expected to produce as good agreement between calculated and experimental values as was obtained with their laboratory-prepared cements.

Plots of the heats of hydration obtained at 7 and 28 days and 1 year in our investigation versus the function % C_3S + 2.1% C_3A are given in figures 5–3, 5–4, and 5–5. The correlation is quite good. The regression equation obtained from our data for the 1-year heat of hydration was as follows:

$$HH(1\ yr) = 58.87 + 0.52\ C_3S + 1.54\ C_3A$$
$$\text{s.d.} = (2.85)(0.053)\quad (0.12)$$

The S.D. for this equation was 3.909, compared to 7.031 for the heat of hydration values. The ratio of 2.9 to 1 in the above equation for the contribution of C_3A verus that of C_3S, compares with the ratio of 2.1 to 1 given by Woods et al.[5] This difference may have been due in part to the difference in curing temperature.

Lerch and Bogue [6] and Thorvaldson et al. [7] have reported values for heat of hydration of the major potential compounds in portland cements, and Lea and Desch, [1, p. 246] quote Brisi [21] as having obtained values of 125 and 63 calories per gram for the heat of hydration of C_3S and C_2S, respectively. Comparing the values which have been reported with the coefficients obtained in the present study for the 1-year heat of

[5] The function given by Woods et al. was obtained by averaging the heats at the various ages for each compound, subtracting the mean value of the heat for C_2S and C_4AF from the values for C_3S and C_3A, and adjusting the values for C_3S and C_3A to a basis of 1.0 for C_3S, maintaining the ratio of 2.1 to 1 between the two.

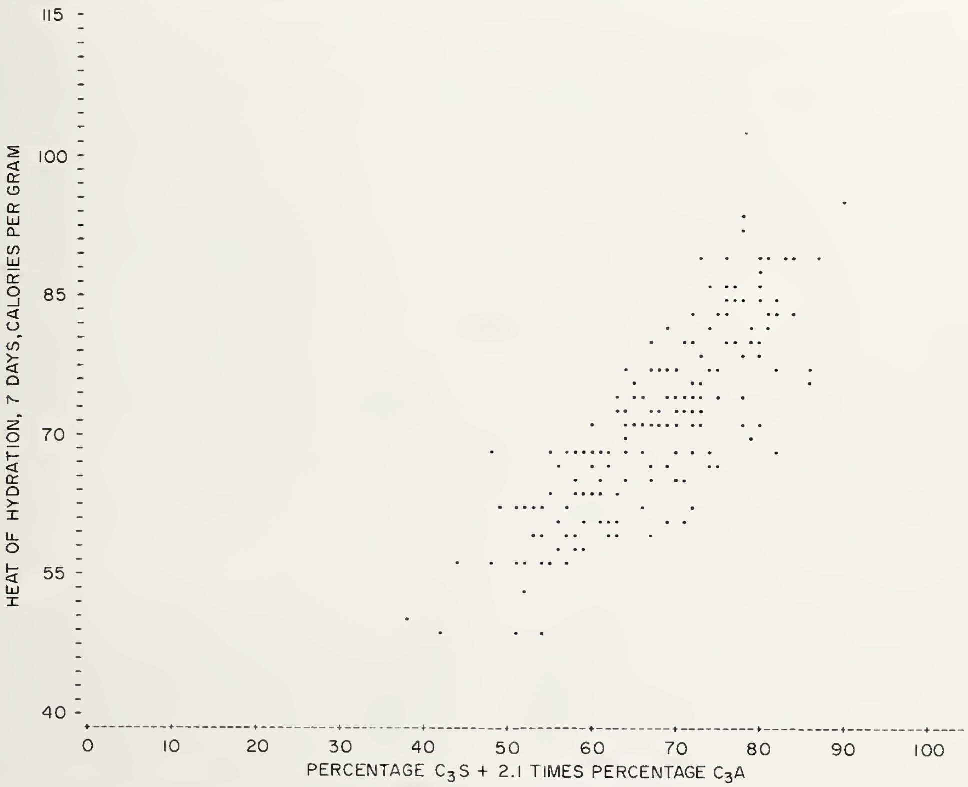

Figure 5–3. *Heat of hydration at 7 days versus the quantity (percentage* C_3S + *2.1* × *percentage* C_3A).

hydration (bar (10) of figure 5–2) it may be noted that the numerical values and 95-percent confidence limits for C_3S and C_4AF are below the respective values of 120 and 100 cal/g reported by Bogue for these compounds. The value for the coefficient for C_2S is close to the value of 62 cal/g reported by Bogue, and the value for C_3A is not significantly different from the value of 207 cal/g reported by Bogue or the value of 214 cal/g reported by Thorvaldson.

5.5. Heat of Hydration and Compressive Strength

It has previously been reported [10] that there was a correlation between the heat of hydration and compressive strength of cements at early ages but not at later ages. A study of variables associated with compressive strength will be presented in a later section of this series of articles. However, table 5–14 presents some computed relationships between the heat of dydration at 7 and 28 days and 1 year versus the compressive strengths of water-cured 2-inch mortar cubes at the respective ages. The "F" values are the ratios of the reduction in variance due to the fitted constants associated with the independent variables to the variance obtained from the residuals after fitting the constants. At 7 days there was a significant relationship between the heat of hydration and strength. At 28 days the reduction in variance was somewhat less but still highly significant whereas at one year there was no apparent correlation between the heat of hydration and compressive strength.

6. Summary and Conclusions

(1) Studies were made of the dependence of the heat of hydration of portland cements on cement composition, including minor constituents and trace elements as well as major potential compounds and major oxides. Heat of solution tests were made at 7 days, 28 days, and 1 year on a large number of portland cements of different types and from different mills in different areas of the United States.

(2) Computations of multivariable equations by a least squares method for air entraining and non-air-entraining cements combined or non-air-entraining cements alone indicated that a number of independent variables are associated either directly or indirectly with the heat of hydration of the cements. The following observations relate to the results obtained with the non-air-entraining cements in which the major potential compounds were used as independent variables.

(2.1) The effect of C_3S and C_2S on the heat

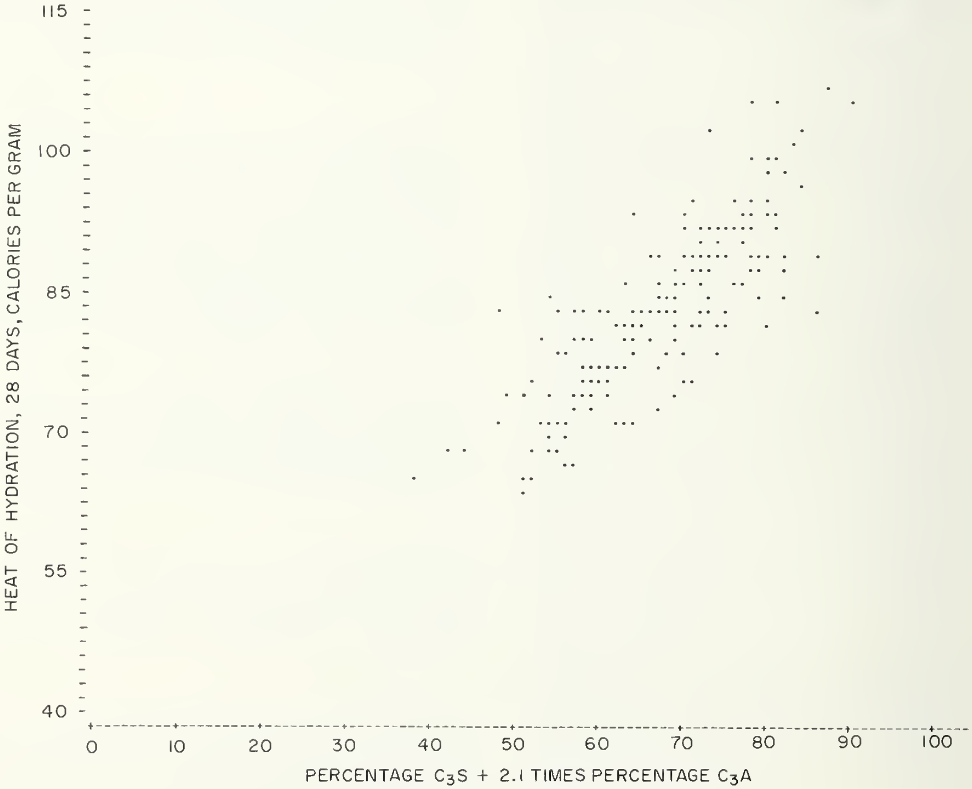

FIGURE 5–4. *Heat of hydration at 28 days versus the quantity (percentage $C_3S+2.1\times$ percentage C_3A).*

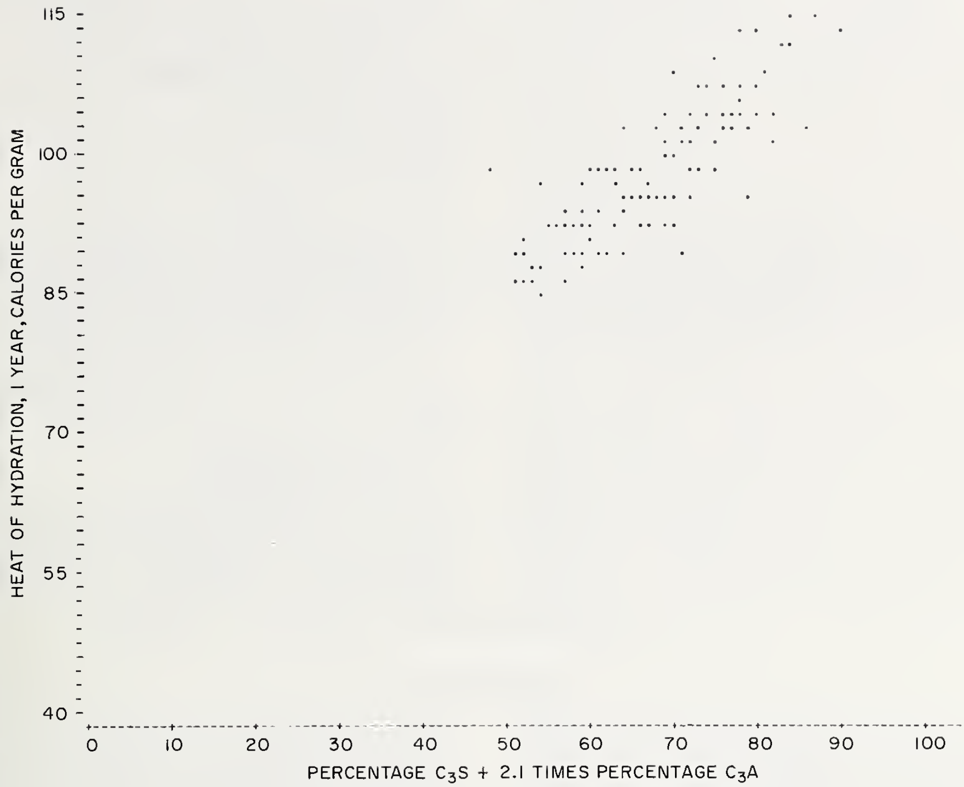

FIGURE 5–5. *Heat of hydration at 1 year versus the quantity (percentage* $C_3S+2.1\times$ *percentage* C_3A*).*

TABLE 5–14. *Coefficients for equations relating heat of hydration to compressive strength at the respective ages and the resulting reduction of variance*

Equation	Type cement	Const.	Compressive strength			S.D.	"F"	D.F.	Critical F	
			7d	28d	1 yr				$\alpha=0.01$	$\alpha=0.05$
1	AE+NAE	HH(7)= +46.24 s.d.= (1.96)	+0.00757 (0.00057)			6.90	86.9	2:170	4.7	3.0
2	do	HH(28)= +53.90 s.d.= (3.36)		+0.00584 (0.00065)		7.63	40.4	2:180	4.7	3.0
3	do	HH(1Y)=+103.4 s.d.= (4.3)			−0.00089 (0.00068)	6.96	0.9	2:133	4.8	3.1
4	NAE	HH(7)= +44.38 s.d.= (2.02)	+0.00801 (0.00059)			6.72	93.5	2:160	4.7	3.0
5	do	HH(28)= +48.96 s.d.= (3.57)		+0.00671 (0.00068)		7.44	48.2	2:170	4.7	3.0
6	do	HH(1Y)=+104.2 s.d.= (5.1)			−0.00103 (0.00079)	6.96	0.8	2:123	4.6	3.1

of hydration increased with the length of hydration. At 1 year it was slightly lower than previously published values for C_3S and did not differ significantly from those values for C_2S. The heat of hydration attributable to C_3A and C_4AF was slightly higher at 28 days than after 7 days or 1 year hydration. All values were within reasonable agreement with previously published values.

(2.2) Of the commonly determined variables, high loss on ignition was associated with low heat of hydration and high fineness was associated with high heat of hydration. High values for K_2O and SO_3 were associated with high heat of hydration at 7 days, but not at later ages. High values for Na_2O were associated with low values of heat of hydration at 1 year, but not at 7 or 28 days.

The use of the commonly determined variables resulted in significantly better agreement between calculated and observed values than was obtained with the four compounds alone.

(2.3) Of the other minor constituents or trace elements, increased values for Cu and P were associated with lower values of heat of hydration at all ages. The relationship with P was highly significant at all ages; that of Cu was more significant at 28 days and 1 year than at 7 days. Increased values for Cr and Zr appeared associated with high heat of hydration at 7 days. At 28 days there was no evidence of a relationship with Cr, and the significance of the Zr was less than at 7 days. Neither of these elements was significant at 1 year. SrO and Co appeared associated with lower heat of hydration at 28 days but not at 7 days or 1 year. At 1 year, increase in V appeared to be related to high heat of hydration and increase in Ba to low heat of hydration but neither of these elements showed any effect at the earlier ages. The use of the minor constituents and trace elements in the equations together with major compounds and commonly determined variables resulted in significantly improved agreement between calculated and observed values.

(3) Inclusion of the air-entraining cements with the non-air-entraining cements did not greatly affect numerical values or significance of the coefficients of the major potential compounds in the equations as compared to those calculated for only the non-air-entraining cements.

(4) Using the major oxides resulted in a series of equations which produced similar reductions in S.D. to those obtained with equations computed for the major potential compounds.

(5) The relationships between heat of hydration and a function of C_3A and C_3S were more dispersed for the commercial cements of this study than for laboratory prepared cements reported in previous studies.

(6) It was verified that there was a highly significant relationship between the heat of hydration at 7 and 28 days and the compressive strength at these ages. There was no apparent correlation between the heat of hydration at 1 year and the 1 year compressive strength.

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Section 6. Variables Associated With Small Autoclave Expansion Values of Portland Cements

R. L. Blaine and H. T. Arni

The autoclave expansion values of the cements in this investigation ranged from minus 0.05 to plus 0.50 percent. Statistical analyses used to determine the variables associated with the expansion confirmed that MgO and C_3A were most significant. Increased values of the alkalies, SrO, V, and loss on ignition were also associated with higher autoclave expansion, whereas increases in SO_3 and Cr were associated with a decrease in the expansion values.

Contents

1. Introduction

The autoclave expansion test has been used in the United States as an accelerated test for soundness of portland and other hydraulic cements for a number of years. H. F. Gonnerman, William Lerch, and Thomas M. Whiteside have presented an extensive review of the literature dealing with the autoclave test and the variables associated with the expansive characteristics of portland cements [1].[1] It is generally recognized that excessive quantities of MgO in the form of periclase as well as "free" lime in portland cements may result in large expansions of the neat cement bars when subjected to the autoclave treatment and, also, may cause excessive expansion and deterioration of concretes stored at normal temperatures. The potential tricalcium aluminate content of the cement has been reported as contributing to the expansion in the autoclave test, but not necessarily to the potential unsoundness or later volume expansion of concrete. It has also been recognized that certain additions to the clinker such as pozzolans (see p. 54 of ref [1]) may reduce the autoclave expansion of the cement to some extent.

Unsoundness of portland cement is associated with autoclave expansion values many times larger than those obtained in this study. However, the contributions of tricalcium aluminate and other factors mentioned above may have a significant effect when expansion values are close to the specification limits. Thus it appeared desirable and feasible to evaluate the contribution of the different variables to the small expansion values obtained on these cements.

2. Materials

The portland cements used in this study are the same as those which have previously been described in sections 1, 2, and 3 of part 1 of this series of papers [2]. These included 199 portland cements of different types and from different areas of the U.S.A., and a few from other countries.

3. Testing Procedure

Neat portland cement pastes of normal consistency were tested in accordance with ASTM [3] and Federal [4] specifications in effect for autoclave expansion of portland cement at the time the tests were made.

The results of tests were analyzed statistically using the same procedures described in section 1, of part 1 of this series [2]. Briefly this consisted of determining by least squares relationships with the principal variables and combinations of variables which were known to be associated with the autoclave expansion of the different cements, and then using various techniques to determine which of additional measured variables appeared to have a significant effect in improving the agreement of actual values and those calculated by the equation.

As in previous sections, the 3 white portland cements and the cement having a high autoclave expansion were not included in the calculated equations.

[1] Figures in brackets indicate the literature references at the end of this section.

4. Results of Tests

The frequency distributions of the different types of cements with respect to autoclave expansion are presented in table 6–1. It may be noted that although an autoclave expansion of 0.50 percent was the specification limit at the time these cements were manufactured, the majority of the cements tested had an expansion of less than 0.10 percent. Most of the cements having 0.25-percent or more expansion were those classified as type I or type IA. Eleven of the cements had negative values for autoclave expansion.

Equations relating the autoclave expansion values to various independent variables are presented in tables 6–2 and 6–3 for the AE+NAE and the NAE cements respectively.[2] In equation 1 of 6–2, with the use of C_3A and $(MgO)^2$ as independent variables, there was a highly significant reduction in the S.D. value.[3] It has previously been established that the use of the second power of MgO resulted in slightly lower S.D. values than was obtained by using the first power (see for example eqs 4 and 5). By use of the alkalies and SO_3 as additional independent variables as in eq 2 there was a further highly significant reduction in the S.D. value. (See also table 6–5 which presents the reduction of "F" values as well as the critical values of "F" at the 0.05 and 0.01 limits.) The addition of the variables, loss on ignition, SrO, V, and Cr values for the cements, as in eq 3, resulted in a further significant reduction in the S.D. values. (See also table 6–5.) The use of the Al_2O_3 and Fe_2O_3 instead of the potential C_3A content as in equations 5, 6, and 7 resulted in a similar series of equations with coefficients and S.D. values comparable with those of equations 1, 2, and 3 respectively.

The calculation of equations for the "odds" and "evens" in the array of cements indicated a fair degree of concordance as may be noted in eqs 7A and 7B. It may be noted that for "Loss" and Cr (coefficients of neither were very highly significant for the entire group of cements, eq 7) the coef./s.d. ratio was less than one in table 6–2, eq 7A for the AE+NAE cements. In table 6–3, eq 7B, the coef./s.d. ratio of Na_2O was less than one whereas the ratios for Loss and Cr were greater than one. Some of the limitations of the methods of statistical analyses used have been presented in previous sections of this series.

In table 6–3 are presented the equations relating the autoclave expansion of the NAE cements to the same independent variables used in table 6–2 for AE+NAE cements. Although there were a few discrepancies as noted previously, the effects of the few AE cements on the coefficients or the S.D. values were not large.

In table 6–4 are presented the calculated contributions of the various independent variables and the ranges of these contributions to the expansion values based on equation 3 of table 6–3. As in previous sections these values must be added to the computed constant and are estimates of the magnitude and range of the contributions of the different variables which may be expected with normal portland cements. Slightly different values would be obtained by use of other equations.

5. Discussion

Expansion values obtained on any sample of cement are usually quite reproducible. It has been reported that the rate of cooling of the cement clinker can greatly affect the expansion values obtained [1]. The rate of cooling of the cement clinkers may differ in different mills, and this is probably one of the factors which masked the contribution of some variables to the volume changes

[2] Abbreviation and notations used in this section are consistent with those used in previous sections. For example AE+NAE refers to the air-entraining plus the non-air-entraining cements, C_3A refers to the potential tricalcium aluminate and "Loss" to the loss on ignition. In addition "Exp" is used in equations to signify the percentage autoclave expansion.

[3] The statistical terms used in this section are consistent with those used in previous sections. For example S.D. refers to the estimated standard deviation calculated from the residuals of a fitted equation, or the estimated standard deviation about the average. Also as in previous sections, s.d. refers to the estimated standard deviation of the coefficient of an independent variable used in a fitted equation, coef./s.d. the ratio of the estimated coefficient (of an independent variable used in an equation) to its estimated standard deviation, and "F"=Fisher's ratio of variances.

TABLE 6–1. *Frequency distribution of cements with respect to autoclave expansion*

Type cement	Percentage autoclave expansion												Total
	−0.05 to 0	0 to 0.05	0.05 to 0.10	0.10 to 0.15	0.15 to 0.20	0.20 to 0.25	0.25 to 0.30	0.30 to 0.35	0.35 to 0.40	0.40 to 0.45	0.45 to 0.50	0.50 to 0.55	
	Number of cements												
I		9	15	17	10	10	7	4	3	3	3		81
IA				3	1	1	1	1				1	8
II	3	35	16	8	2	2			1				67
IIA			1	2									3
III	4	6	8	1			1						20
IIIA			2	1									3
IV & V	4	8		3									15
Total	11	58	42	35	13	13	9	5	4	3	3	1	197

TABLE 6–2. *Coefficients for equations relating autoclave expansion of AE+NAE cements to various independent variables*

Equation	Note	Const.	Al_2O_3	Fe_2O_3	C_3A	MgO	$(MgO)^2$	Na_2O	K_2O	SO_3	Loss	SrO	V	Cr	S.D.
1	(1)	Exp. = −0.1244 s.d. = (0.0174)			+0.0213 (0.0019)		+0.0076 (0.0010)								0.0780
2	(1)	Exp. = −0.1126 s.d. = (0.0314)			+0.0195 (0.0020)		+0.0070 (0.0010)	+0.1107 (0.0340)	+0.0810 (0.0284)	−0.0280 (0.0172)					0.0745
3	(1)	Exp. = −0.1035 s.d. = (0.0338)			+0.0181 (0.0022)		+0.0069 (0.0009)	+0.0779 (0.0337)	+0.0814 (0.0269)	−0.0493 (0.0176)	+0.0181 (0.0107)	+0.2501 (0.0699)	+1.063 (0.340)	−2.559 (1.363)	0.0698
4	(1)	Exp. = −0.1778 s.d. = (0.0460)	+0.0566 (0.0061)	−0.0307 (0.0081)		+0.0374 (0.0051)									0.0795
5	(1)	Exp. = −0.1561 s.d. = (0.0446)	+0.0589 (0.0060)	−0.0302 (0.0080)			+0.0077 (0.0010)								0.0782
6	(1)	Exp. = −0.1213 s.d. = (0.0494)	+0.0524 (0.0066)	−0.0313 (0.0077)			+0.0070 (0.0010)	+0.1104 (0.0341)	+0.0798 (0.0291)	−0.0281 (0.0173)					0.0748
7	(1)	Exp. = −0.1076 s.d. = (0.0511)	+0.0483 (0.0072)	−0.0298 (0.0073)			+0.0069 (0.0009)	+0.0780 (0.0338)	+0.0810 (0.0275)	−0.0494 (0.0177)	+0.0182 (0.0107)	+0.2488 (0.0712)	+1.068 (0.346)	−2.576 (1.370)	0.0700
7A	(2)	Exp. (odd) = −0.1350 s.d. = (0.0770)	+0.0443 (0.0105)	−0.0171 (0.0111)			+0.0075 (0.0013)	+0.0840 (0.0461)	+0.0612 (0.0429)	−0.0392 (0.0301)	*+0.0038 (0.0165)	+0.2762 (0.1076)	+0.899 (0.499)	*−1.572 (1.902)	0.0719
7B	(2)	Exp. (even) = −0.0872 s.d. = (0.0768)	+0.0533 (0.0107)	−0.0409 (0.0107)			+0.0066 (0.0015)	+0.0825 (0.0538)	+0.0774 (0.0422)	−0.0529 (0.0229)	+0.0285 (0.0150)	+0.2256 (0.1068)	+1.233 (0.505)	−4.356 (2.196)	0.0703

[1] 178 cements, avg. = 0.1073, S.D. = 0.1158. [2] 89 cements. *Coefficient/s.d. ratio less than 1.

TABLE 6–3. *Coefficients for equations relating autoclave expansion of NAE cements to various independent variables*

Equation	Note	Const.	Al_2O_3	Fe_2O_3	C_3A	MgO	$(MgO)^2$	Na_2O	K_2O	SO_3	Loss	SrO	V	Cr	S.D.
1	(1)	Exp. = −0.1269 s.d. = (0.0178)			+0.0214 (0.0019)		+0.0079 (0.0010)								0.0786
2	(1)	Exp. = −0.1194 s.d. = (0.0328)			+0.0196 (0.0021)		+0.0072 (0.0010)	+0.1143 (0.0348)	+0.0820 (0.0294)	−0.0258 (0.0179)					0.0749
3	(1)	Exp. = −0.1146 s.d. = (0.0350)			+0.0185 (0.0022)		+0.0071 (0.0010)	+0.0810 (0.0342)	+0.0782 (0.0277)	−0.0478 (0.0181)	+0.0213 (0.0110)	+0.2601 (0.0724)	+1.086 (0.344)	−2.643 (1.404)	0.0699
4	(1)	Exp. = −0.1743 s.d. = (0.0474)	+0.0566 (0.0063)	−0.0323 (0.0084)		+0.0385 (0.0053)									0.0803
5	(1)	Exp. = −0.1516 s.d. = (0.0460)	+0.0588 (0.0062)	−0.0318 (0.0082)			+0.0079 (0.0010)								0.0788
6	(1)	Exp. = −0.1228 s.d. = (0.0512)	+0.0521 (0.0068)	−0.0324 (0.0079)			+0.0073 (0.0010)	+0.1142 (0.0350)	+0.0816 (0.0301)	−0.0259 (0.0180)					0.0753
7	(1)	Exp. = −0.1128 s.d. = (0.0528)	+0.0488 (0.0073)	−0.0315 (0.0074)			+0.0071 (0.0010)	+0.0810 (0.0344)	+0.0785 (0.0283)	−0.0478 (0.0183)	+0.0214 (0.0111)	+0.2605 (0.0737)	+1.084 (0.349)	−2.661 (1.411)	0.0702
7A	(2)	Exp. (odd) = −0.1427 s.d. = (0.0747)	+0.0469 (0.0106)	−0.0160 (0.0119)			+0.0080 (0.0013)	+0.0921 (0.0463)	+0.0492 (0.0415)	−0.0616 (0.0278)	+0.0296 (0.0211	+0.3561 (0.1207)	+0.822 (0.499)	−2.509 (1.993)	0.0724
7B	(2)	Exp. (even) = −0.1115 s.d. = (0.0818)	+0.0514 (0.0110)	−0.0411 (0.0100)			+0.0062 (0.0015)	*+0.0515 (0.0574)	+0.0981 (0.0443)	−0.0349 (0.0268)	+0.0186 (0.0143)	+0.2357 (0.1104)	+1.218 (0.525)	−2.724 (2.190)	0.0700

[1] 167 cements, avg. = 0.104, S.D. = 0.1170. [2] 83 or 84 cements. *Coefficient/s.d. ratio less than 1.

Table 6–4. *Calculated contributions of independent variables to the autoclave expansion of neat portland cements*

Independent variable	Range of variable (percent)	Coefficients from eq 3, table 6–3	Calculated contribution to expansion	Calculated range of contribution to expansion
			Const. −0.1146	
C_3A	1 to 15	+0.0185	+0.02 to +0.28	0.26
$(MgO)^2$	0 to 25	+0.0071	0 to +0.18	0.18
Na_2O	0 to 0.7	+0.0810	0 to +0.06	0.06
K_2O	0 to 1.0	+0.0782	0 to +0.08	0.08
SO_3	1.2 to 3.6	−0.0478	−0.06 to −0.17	0.11
Loss	0.3 to 3.6	+0.0213	+0.01 to +0.08	0.07
SrO	0 to 0.35	+0.2601	0 to +0.10	0.10
V	0 to 0.1	+1.086	0 to +0.10	0.10
Cr	0 to 0.02	−2.643	0 to −0.05	0.05

Table 6–5. *"F" values for significance of reduction of variance due to added variables.*

Table	Equations	"F" ratio	D.F.	Critical "F" ratio	
				$\alpha=0.01$	$\alpha=0.05$
6–2	0 and 1	72.44	3:175	3.88	2.68
Do	1 and 2	6.61	3:172	3.88	2.68
Do	2 and 3	6.99	4:168	3.43	2.43
Do	0 and 5	54.08	4:174	3.43	2.43
Do	5 and 6	6.39	3:171	3.88	2.68
Do	6 and 7	7.06	4:167	3.43	2.43
6–3	0 and 1	68.68	3:164	3.88	2.68
Do	1 and 2	6.53	3:161	3.88	2.68
Do	2 and 3	6.96	4:157	3.43	2.43
Do	0 and 5	51.29	4:163	3.43	2.43
Do	5 and 6	6.17	3:160	3.88	2.68
Do	6 and 7	7.02	4:156	3.43	2.43

obtained. Another of the unknown variables was the quantity of "free" lime in the different cements. However, the present tests confirmed that C_3A and MgO are both significantly related to the small expansion values obtained. The coef./s.d. ratios of most of the minor constituents were not highly significant. This may have resulted from the masking effect of the other unknown variables. Judging from the equations in tables 6–2 and 6–3, and from the calculated contributions of the different variables to the expansion as presented in table 6–4, it would appear that the increase in total alkalies as well as the V and SrO tend to increase the expansion whereas the increase of SO_3 content (in the rather low percentages present in these cements) tends to cause a decrease of the autoclave expansion values. No information was available on the effect of the "optimum" amount of SO_3 or of more than the optimum which may result in expansion and deterioration of concrete at normal temperatures.

6. Summary and Conclusions

The autoclave expansion values of the cements used in this investigation ranged from 0.50 to minus 0.05 percent. Most of the cements had an autoclave expansion of less than 0.10 percent. Cements classified as type I and type IA accounted for most of the higher expansion values.

Statistical analyses by the least squares method were used to investigate the variables associated with the small volume changes. It was confirmed that the MgO and C_3A were the most significant variables involved. Increase in the content of alkalies, both sodium and potassium, as well as an increase in SrO, V, and loss on ignition were also associated with higher autoclave expansion values whereas an increase in the SO_3 and Cr contents were associated with lower autoclave expansion values. Lack of information on the rate of cooling of the different cement clinkers and of the free lime contents of the cements may have masked the effect of other variables.

7. References

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[2] Interrelations between Cement and Concrete Properties, Part 1 NBS Building Science Series No. 2. Section 1—Materials and Techniques. Section 2—Water Requirements of Portland Cements. Section 3—Occurrence of Minor and Trace Elements in Portland Cement.

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[4] Federal Specification SS–C–158c Amendment 1; Cements, Hydraulic, Methods for Sampling, Inspection and Testing, May 25, 1954.

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U.S. GOVERNMENT PRINTING OFFICE: 1966 O—208-577

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