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## EFFECT OF CALCIUM CHLORIDE ON PORTLAND CEMENTS AND CONCRETES

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### ABSTRACT

To study the effect of the addition of calcium chloride on portland cements of widely varying composition, and on portland-cement concretes, a carefully controlled laboratory investigation was conducted. Such measurements as heats of hydration, setting times, consistencies and the strengths at various ages under several curing temperatures were made.

The addition of calcium chloride appears to increase somewhat the heat contributed at the end of 24 hours by dicalcium silicate and tetracalcium aluminoferrite and to decrease the heat contributed by tricalcium aluminate. Calcium chloride has but little effect on the heat contributed by tricalcium silicate. Calcium chloride increases the rate at which the heat is evolved from all cements. The strength contributed by the two silicate compounds in cement was increased and the strength contributed by tricalcium aluminate was decreased by the addition of calcium chloride. Calcium chloride decreased the time of set of 11 commercial cements and increased the flow and the strength of the resulting concrete. The physical properties of the experimental cements were similarly affected by the addition of calcium chloride. The optimum amounts to be added for different types of cement and at various curing temperatures are indicated.

### CONTENTS

	Page
I. Introduction.....	499
II. Description of cements and calcium chloride.....	500
III. Effect of calcium chloride on the heat evolved during the first 24 hours of hydration.....	500
1. Heat of hydration of experimental cements.....	500
2. Heat of hydration of 11 commercial cements.....	502
IV. Effect of calcium chloride on the physical properties of mortars and concretes.....	504
1. Strength of experimental cements.....	504
2. Commercial cements.....	508
(a) Making the test specimens.....	508
(b) Test results.....	508
(1) Time of set.....	508
(2) Strengths.....	509
(3) Plasticity tests.....	512
V. Discussion and recommendations.....	513
VI. Summary.....	515
VII. References.....	517

### I. INTRODUCTION

The Calcium Chloride Association, through its research fellowship at the National Bureau of Standards, has been investigating the effect of calcium chloride on portland cement and portland-cement

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concrete. The investigation included a study of the influence of calcium chloride on the heat evolved up to 24 hours, and on the strength developed, by the major compounds present in portland cement. The comparative properties of mortars and concretes with different percentages of calcium chloride and at curing temperatures of 40, 70, and 90° F were also studied.

A progress report on these studies was presented at the thirteenth annual meeting of the Highway Research Board (1),<sup>2</sup> and a final report is given in this paper. A physico-chemical study of the reaction of calcium chloride with the alumina compounds of portland cement is being made, and will be reported separately.

## II. DESCRIPTION OF CEMENTS AND CALCIUM CHLORIDE

Eight commercial portland cements (referred to in this paper as standard cements) together with one high-early-strength and two white portland cements were studied. In selecting these cements an effort was made to obtain the greatest practical variation in composition and physical properties.

Sixty experimental cements of varying composition and four commercial portland cements were furnished by the Portland Cement Association Fellowship at the National Bureau of Standards for certain heat and strength studies.<sup>3</sup> In the text of this report the cement compounds are abbreviated as follows:

Compound	Chemical formula	Abbreviation
Tricalcium silicate.....	$3\text{CaO} \cdot \text{SiO}_2$ .....	$\text{C}_3\text{S}$
Dicalcium silicate.....	$2\text{CaO} \cdot \text{SiO}_2$ .....	$\text{C}_2\text{S}$
Tricalcium aluminate.....	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$ .....	$\text{C}_3\text{A}$
Tetracalcium aluminoferrite.....	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ .....	$\text{C}_4\text{AF}$

Each of the cements furnished by the Portland Cement Association was ground to such a fineness that 12.5 percent was retained on the no. 200 sieve.

The calcium chloride used was a commercial product complying with the American Society for Testing Materials' Standard Specification D98-34. The amounts added to the cement are reported as percentages of anhydrous calcium chloride by weight of cement.

## III. EFFECT OF CALCIUM CHLORIDE ON THE HEAT EVOLVED DURING THE FIRST 24 HOURS OF HYDRATION

### 1. HEAT OF HYDRATION OF EXPERIMENTAL CEMENTS

The samples of experimental cements had a wide range in composition, which made them of especial value in the present study. The analytical data and heats of hydration in the absence of calcium chloride were kindly furnished by the Portland Cement Association Fellowship. The quantity of each cement available was so limited that only one additional calorimetric determination (using one percent of anhydrous calcium chloride) could be made.

<sup>2</sup> Figures in parentheses here and elsewhere in the text refer to the references at the end of this paper.

<sup>3</sup> Table of the analyses of these cements as well as details of all the data will be published in the proceedings of the fourteenth annual meeting of the Highway Research Board.

The apparatus used for measuring directly the heat of hydration was that developed at the National Bureau of Standards (2).

The cement (200 grams) and water (67.5 grams) were thoroughly mixed in a small tinned can by a high-speed stirring device. Copper-constantan thermocouples were inserted into the mixture and the can was placed in a double-walled vacuum flask, which was in turn tightly closed and placed in an air thermostat maintained at 21° C. The temperatures were recorded by a multiple-junction recording potentiometer.

From the data obtained in this manner it was possible to calculate the heat evolved by the cement at any given period (3) in the 24 hour interval, having made the necessary correction for the radiation loss of the vacuum flask and its contents.

TABLE 1.—*Contribution of individual compounds to heat of hardening at 24 hours*

(Expressed as calories for each percent in 1 gram of cement)

Compound	Without CaCl <sub>2</sub>	Probable error	With the addition of 1% CaCl <sub>2</sub> <sup>a</sup>	Probable error
Tricalcium silicate.....	.80	± .02	.78	± .02
Dicalcium silicate.....	.19	± .02	.26	± .02
Tricalcium aluminate.....	1.62	± .07	1.47	± .06
Tetracalcium aluminoferrite.....	.01	± .08	.25	± .06

<sup>a</sup> 1% anhydrous CaCl<sub>2</sub>=1.3% commercial CaCl<sub>2</sub>.

The contributions of the individual compounds to the heat of hardening were calculated, for the 60 experimental cements, by the method of least squares from the percentages of the compounds in the cements computed by the method of Bogue (4), assuming that a linear relationship exists between the compound composition of the cement and the heat evolved. The values obtained from these cements (table 1) show the same trends as those reported by Blank (5) and by Wood and coworkers (6), namely, that tricalcium aluminate evolves the greatest heat (expressed in calories for each percent present in each gram of cement), tricalcium silicate being next in order. The addition of calcium chloride increased somewhat the heat contributed by dicalcium silicate and tetracalcium aluminoferrite, had little or no effect on the heat contribution of tricalcium silicate, and decreased the heat contributed by tricalcium aluminate. The factors for the major cement compounds may be used to obtain a fairly accurate estimate of the increase in the rate of evolution of heat and the total heat evolved up to 24 hours for a particular cement when calcium chloride is added.

In order to illustrate the effect of change in compound composition upon the heat developed when calcium chloride is present table 2 was prepared. Column 1 of the table gives the grouping, column 2 the number of cements in each group, column 3 the average change in the heat developed in 24 hours produced by the addition of 1 percent of calcium chloride, and the remaining 4 columns the average compound composition. From this table it can be seen for the experimental cements that an increase in the heat evolved from group to group was accompanied by an increase in percentage of both the tricalcium aluminate and the tricalcium silicate, the two compounds shown from

table 1 to be those contributing the greater quantities of heat of hydration.

TABLE 2.—Changes in the total heat evolved at 24 hours by the addition of 1 percent of calcium chloride to experimental cements

Heat evolved in 24 hours without $\text{CaCl}_2$	Number of cements group	Average changes produced by 1% $\text{CaCl}_2^a$	Average compound composition			
			Tricalcium aluminate	Tetra-calcium aluminoferrite	Dicalcium silicate	Tricalcium silicate
cal/g		cal/g	Percent	Percent	Percent	Percent
30 to 40.....	9	+7	3	15	47	30
40 to 50.....	12	+5	4	14	35	42
50 to 60.....	24	+4	10	12	34	42
60 to 70.....	16	0	10	11	25	52
70 to 80.....	3	-2	15	7	21	53

<sup>a</sup> 1% of anhydrous  $\text{CaCl}_2$  = 1.3% of commercial  $\text{CaCl}_2$ .

Furthermore, the increase in the heat evolved because of the addition of 1 percent of calcium chloride is greatest in the first group (cements of lowest heat), becomes less in the succeeding groups, reaches zero in the fourth group, and in the fifth group there is actually a decrease of 2 calories per gram. These changes in heat evolved because of the addition of calcium chloride cannot apparently be assigned to the tricalcium silicate content in each group, since it has been shown in table 1 that each percent of tricalcium silicate present in 1 gram of cement evolves the same number of calories with or without calcium chloride. The changes do, however, appear to be inversely related to the amounts of tricalcium aluminate, and directly related to those of dicalcium silicate and tetracalcium aluminoferrite present in each group, and in this respect are in agreement with the data of table 1.

## 2. HEAT OF HYDRATION OF 11 COMMERCIAL CEMENTS

The heats evolved during the first 24 hours of hydration were measured for 11 commercial cements without calcium chloride and also with the addition of 0.5, 1, 1.5, and 2 percent of anhydrous calcium chloride.

The heat data obtained from the 11 commercial cements, and from 4 samples of commercial cement supplied by the Portland Cement Association Fellowship, were analyzed in the same manner as the data obtained from the experimental cements. The results of the analysis showed that the heat contribution of the individual compounds, and the effect on the heat when calcium chloride was added, were much the same for these commercial cements as for the experimental cements.

The effect of the addition of calcium chloride on the heat developed by a typical portland cement (B) is shown in figure 1. As the amount of calcium chloride is increased, the initial rate of evolution of heat is increased, but the amount of heat developed at 24 hours does not differ by more than a few calories. The other 7 standard and the 2 white portland cements behave in a similar manner upon the addition of calcium chloride.



Time-heat curves plotted from the temperature data of these cements show that calcium chloride generally increases the initial

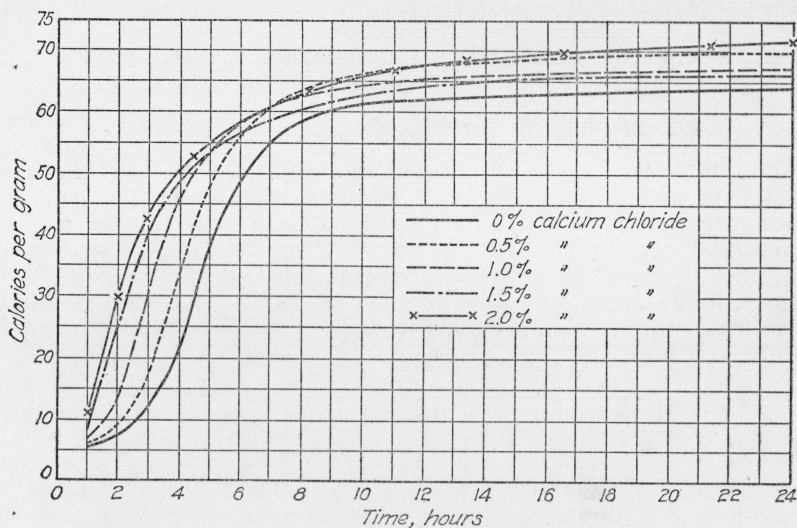


FIGURE 1.—Typical heat curves.

(Cement B).

rate of temperature rise and decreases the time required to reach the maximum temperature. However, with the high-early-strength

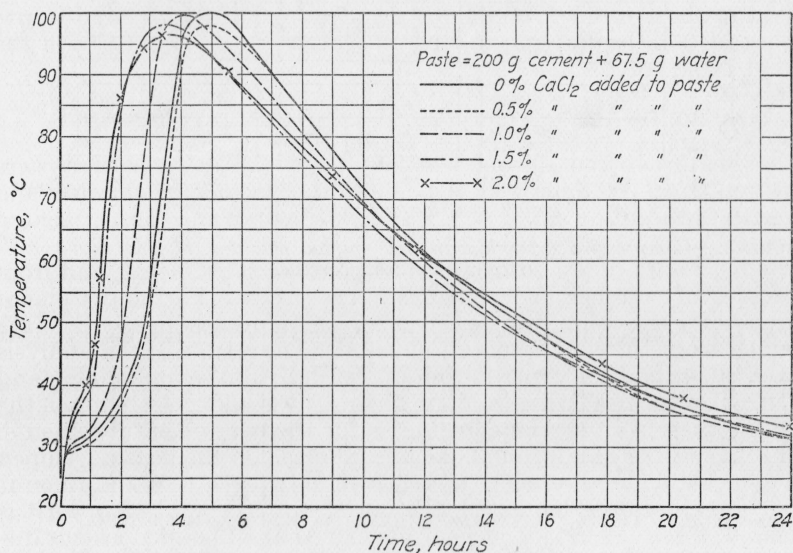


FIGURE 2.—Temperature curves for high-early-strength cement.

(Cement D)

cement (fig. 2), both with and without calcium chloride, the maximum temperature attained was at or near the boiling point of water.

Consequently the heat of hydration could not be ascertained satisfactorily since an undetermined portion of the heat was lost as the latent heat of vaporization of the water evaporated.

#### IV. EFFECT OF CALCIUM CHLORIDE ON THE PHYSICAL PROPERTIES OF MORTARS AND CONCRETES

##### 1. STRENGTH OF THE EXPERIMENTAL CEMENTS

The quantity of each cement was so small that only 1-inch cubes for 3 ages and 3 percentages of admixture could be made. The cubes were made of a 1:2.75 pit-run Ottawa-sand mortar with a cement-water ratio of 1.73 by weight, and contained respectively 0, 1, and 2 percent of anhydrous calcium chloride by weight of the cement. The specimens were molded at 70° F, placed in a moist closet for 24 hours, then removed from the molds and stored in water at 70° F until tested.

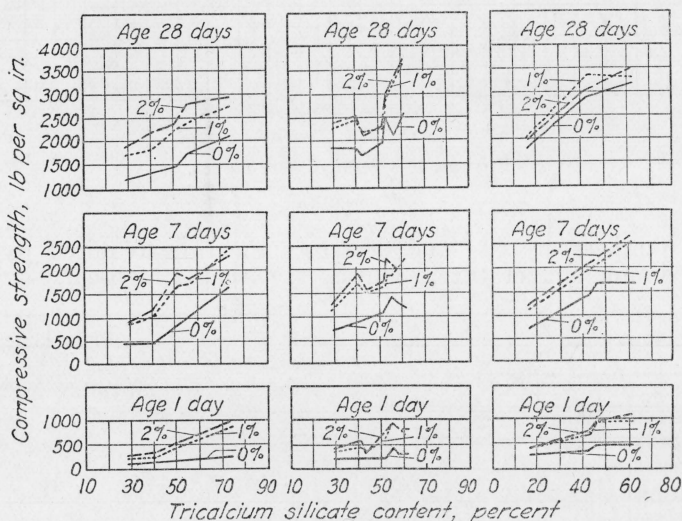


FIGURE 3.—Compressive strength with and without calcium chloride with variable tricalcium silicate content.

Cement no.	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	Cement no.	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	Cement no.	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF
45	28	52	0	15	41	29	49	7	12	37	16	58	16	6
6	41	39	0	14	24	41	37	7	12	8a	42	33	15	7
11	51	29	0	15	4	43	34	7	13	57	45	28	15	7
46	56	24	0	16	59	52	26	6	13	38	61	14	14	7
61	56	24	0	16	9	53	25	7	13	58	62	13	14	7
62	74	5	0	15	60	55	20	7	12					
					60a	57	20	6	13					
					42	61	17	7	12					

C<sub>3</sub>A=0%; C<sub>4</sub>AF=14 to 16%      C<sub>3</sub>A=6 to 7%; C<sub>4</sub>AF=12 to 13%      C<sub>3</sub>A=14 to 16%; C<sub>4</sub>AF=6 to 7%

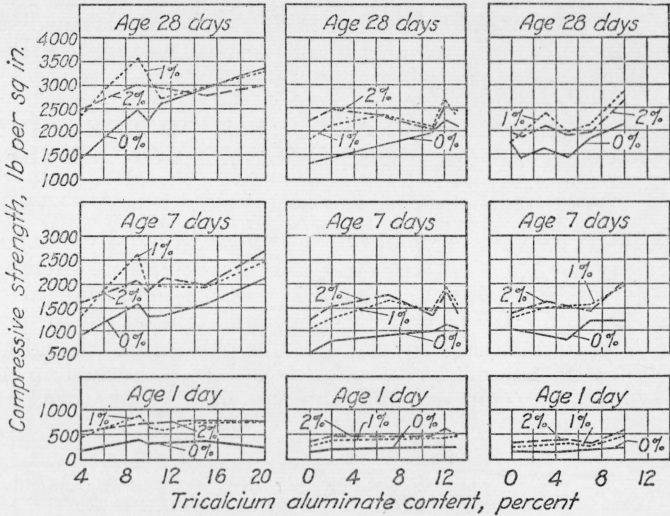


FIGURE 4.—Compressive strength with and without calcium chloride with variable tricalcium-aluminate content.

Cement no.	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	Cement no.	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	Cement no.	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF
50	47	37	4	8	6	41	39	0	14	19	44	33	0	19
16	42	38	9	6	51	38	45	2	13	27	41	35	1	20
53	47	35	10	4	4	43	34	7	13	17	39	37	3	18
28	44	34	11	6	24	41	37	7	12	23	38	33	5	20
57	45	28	15	7	29	40	33	11	13	13	38	31	7	21
8a	42	33	15	7	12	41	32	12	12	21	40	30	10	17
1a	45	28	20	4	20	42	30	12	13					
					30	39	32	13	13					
C <sub>4</sub> AF=4 to 8%					C <sub>4</sub> AF=12 to 14%					C <sub>4</sub> AF=17 to 21%				

The strength results in figures 3, 4, and 5, and published tests by other investigators, reveal that the compressive strength of mortars is markedly influenced by the chemical composition of the cement. This is to be expected in view of the fact that the individual compounds have entirely different strength characteristics, and their proportions in the cement affect the strength of the whole.

The findings of this investigation corroborate, in general, the results reported by Gonnerman (7) on practically the same cements, namely, (a) "The principal strength contributing compounds of portland cement are tricalcium and dicalcium silicates. Tricalcium silicate not only contributed much of the strength at the early ages but also continued to be effective in increasing the strength at the later ages. Dicalcium silicate contributed little to the strength up to 28 days, but was largely responsible for the increase in strength beyond this period; (b) tricalcium aluminate contributed strength to an important degree up to 28 days, but its effect then diminished and became zero or negative at 1 and 2 years, and (c) the role of tetracalcium alumino-ferrite is not so clearly indicated. It contributed to some extent to the compressive strength of mortars and concrete at 28 days and later periods."

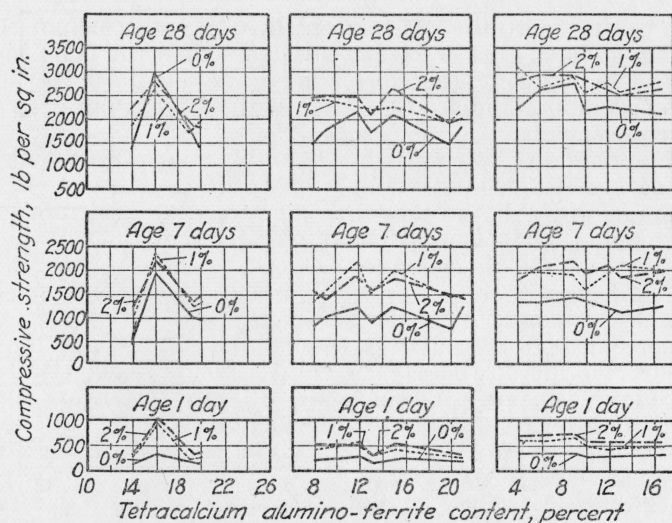


FIGURE 5.—Compressive strength with and without calcium chloride with variable tetracalcium aluminoferrite content.

Cement no.	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	Cement no.	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	Cement no.	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF
6	41	39	0	14	50	47	37	4	8	53	47	35	10	4
58	39	40	2	16	18	43	39	5	9	28	44	34	11	6
19	44	33	0	19	24	41	37	7	12	34	41	36	11	9
27	41	35	1	20	4	43	34	7	12	35	41	33	11	9
					14	37	38	7	15	3b	43	33	11	10
					22	41	33	8	15	12	41	32	12	12
					23	38	33	5	20	20	42	30	12	13
					13	38	31	7	21	21	40	31	10	17

C<sub>3</sub>A=0 to 2%

C<sub>3</sub>A=4 to 8%

C<sub>3</sub>A=10 to 12%

The relation between the silicate content of the cements and the compressive strength of the mortars, with and without calcium chloride, is shown in figure 3. The cements tested had a computed C<sub>3</sub>S content ranging from 16 to 74 percent by weight and a C<sub>2</sub>S content ranging from 5 to 53 percent. With the amounts of the other compounds maintained essentially constant, an increase or decrease in the C<sub>3</sub>S content was accompanied by a decrease or increase in the C<sub>2</sub>S content. The results (fig. 3) show that the addition of calcium chloride increased the mortar compressive strength at all ages of all the cements covering the exceedingly wide ranges in silicate content noted above.

The relation between the content of tricalcium aluminate and the compressive strength of the cement mortars, with and without calcium chloride, is given in figure 4. In order to study the effect of the C<sub>3</sub>A content on strength, 3 groups of cements were selected in which the C<sub>3</sub>A content varied, but the C<sub>3</sub>S, C<sub>2</sub>S, and C<sub>4</sub>AF contents were held as constant as possible in each group. The C<sub>4</sub>AF varied from group to group. A study of the data, (fig. 4), reveals that the action of calcium chloride on the C<sub>3</sub>A does not affect the strength to any great extent until the C<sub>3</sub>A content is increased beyond the amount encountered in commercial portland cements. Carlson and Bates (8) found the average amount of C<sub>3</sub>A in 84 commercial cements to be 11 percent, ranging from 4 to 17 percent. Only 6 of the experimental cements had a C<sub>3</sub>A content of 15 percent or more. Three of the



cements having more than 15 percent of  $C_3A$  with calcium chloride added (fig. 4) have greater 28-day strengths than the plain mortars. It is considered unlikely, therefore, that the action of calcium chloride on the tricalcium aluminate would affect the strength of present-day commercial cements.

Results of tests of calcium chloride on 3 groups of cements, each containing nearly constant amounts of  $C_3S$ ,  $C_2S$ , and  $C_3A$ , but variable amounts of  $C_4AF$ , indicate that the presence of calcium chloride in the amounts studied increased the strength of the cements until the percentage of  $C_4AF$  was above 13 (fig. 5). Referring again to the data of Carlson and Bates (8) we find that the average amount of  $C_4AF$  in 84 commercial portland cements was 8 percent, ranging from 2 percent to 13 percent. Beyond 13 percent of  $C_4AF$  the action of calcium chloride on the experimental cements is not clearly indicated. Three cements containing 16, 19, and 20 percent of  $C_4AF$  have a lower strength at 28 days with calcium chloride, but 5 cements containing more than 13 percent of  $C_4AF$  have a greater strength with calcium chloride.

A mathematical analysis of the compressive-strength data reveals more clearly the effect of calcium chloride on the strength-contributing value of the individual compounds. The results of this analysis made by the method of least squares give factors (table 3) showing the contribution in pounds per square inch for each percent of the 4 major compounds. The analysis assumes a linear relationship between the percentage of each compound and the strength at a given age.

TABLE 3.—Component compressive-strength factors, with and without calcium chloride, for sixty experimental cements

CaCl <sub>2</sub>	Age	Strength factors (pounds per square inch for each percent of component)				Difference between calculated and observed strengths, <sup>1</sup> expressed as probable error	
		$C_3S$	$C_2S$	$C_3A$	$C_4AF$	lb/in. <sup>2</sup>	Percent
Percent	Days						
0	1	4.09±0.36	0.22±0.38	10.4±1.1	-2.7±1.2	±37	16
1		13.03±0.79	-1.03±0.83	15.1±2.3	-10.9±2.7	±81	14
2		13.91±0.61	-1.06±0.65	16.2±1.8	-8.7±2.1	±63	10
0	7	20.8±1.2	-4.1±1.2	47.6±3.4	-0.2±3.9	±119	10
1		31.8±1.6	0.2±1.7	41.3±4.9	-1.2±5.5	±168	10
2		33.7±1.5	3.4±1.5	33.1±4.4	-7.0±5.0	±151	9
0	28	30.2±1.6	3.9±1.6	88.9±4.6	-3.6±5.3	±160	8
1		41.2±1.9	13.8±2.1	58.1±5.8	-12.6±6.6	±201	8
2		46.1±1.9	16.0±2.0	38.5±5.7	-18.8±6.5	±197	8

<sup>1</sup> For each cement the strength was calculated from the factors. The probable errors given are computed from the difference ( $d$ ) between the calculated and observed strengths for each cement by the equation: Probable error =  $.6745\sqrt{\frac{\sum d^2}{n-1}}$

Tricalcium silicate adds strength to the cements at all ages. Calcium chloride is effective in increasing the strength-contributing value of  $C_3S$  in cement at all ages tested. At 1 day the  $C_2S$  contributes little or nothing to the strength. At 7 days the effect is negative, but at 28 days there is a gain of approximately 4 lb/in.<sup>2</sup> for each percent. The addition of calcium chloride increases the strength-contributing factor of the  $C_2S$  at the ages studied although it shows little effect at 1 day. At 7 days 2 percent of anhydrous calcium

chloride increases the strength by about 7 lb/in.<sup>2</sup> for each percent of C<sub>2</sub>S, and at 28 days this strength is increased by about 12 lb/in.<sup>2</sup>

Tricalcium aluminate adds to the strength at all ages up to 28 days. Calcium chloride increases the strength contributed by C<sub>3</sub>A at 1 day, but it decreases the strength at 7 and 28 days. The decrease is larger with increasing amounts of calcium chloride and is largest at 28 days.

The strength contributed by C<sub>4</sub>AF is so small and the probable error is such that it is not known whether the contribution is positive or negative at any age. The addition of calcium chloride apparently makes these factors negative.

Using the factors which give the strength contributed by the four major compounds in cement, and knowing the compound composition of the cement, a fairly accurate computation of the strength produced by the addition of calcium chloride can be obtained. Referring to table 3 we see that the strength can be calculated for all cases, with probable errors ranging from 8 to 16 percent. With 2 percent of anhydrous calcium chloride the precision of the computed strength varies from 8 to 10 percent.

## 2. COMMERCIAL CEMENTS

### (a) MAKING THE TEST SPECIMENS

The standard evaluation tests for portland cement (9) were made, except that 2-inch mortar cubes were substituted for briquettes. In these tests 0, 0.5, 1, 1.5, and 2 percent of anhydrous calcium chloride, respectively, were added to the gaging water. The mortar specimens were molded at 70° F, placed in a moist closet at 70° F for the first 24 hours, removed and stored in water at the same temperature until tested.

Concrete was tested in the form of 6 by 12-inch cylinders made from a 1:2:4 mix by volume, using local sand and gravel. The amount of water (6.5 gallons per sack) used for gaging gave a cement-water ratio of 1.73 by weight and contained, respectively, 0, 1, 1.5, and 2.25 percent of anhydrous calcium chloride by weight of the cement.

The effect of three curing temperatures on strength was studied by means of plastic mortar tests (10) which were designed to give mortar strengths comparable with those of concrete. Pit-run Ottawa sand was used as the aggregate in the proportion of 1 part of cement to 2.65 parts of sand. The same cement-water ratio and percentages of admixtures of calcium chloride were used as in the concrete tests. The mortar specimens were cured 1 day in the molds at 70, 40, and 90° F. then removed from the molds and stored in water. The curing conditions were:

Storage 1.—Cured at 70° F for 90 days (standard).

Storage 2.—Cured at 40° F for first 28 days, then 70° F.

Storage 3.—Cured at 90° F for first 28 days, then 70° F.

### (b) TEST RESULTS

(1). *Time of Set*.—A summary of the setting times for the standard portland cements is shown in figure 6. It will be noted that the average setting time together with, in general, the spread of the time of set, decreases as the amount of calcium chloride is increased. The addition of calcium chloride to the white and high-early-strength

cements, likewise decreases the time of set. All pats, subjected to 5 hours' steaming, both with and without calcium chloride, were sound.

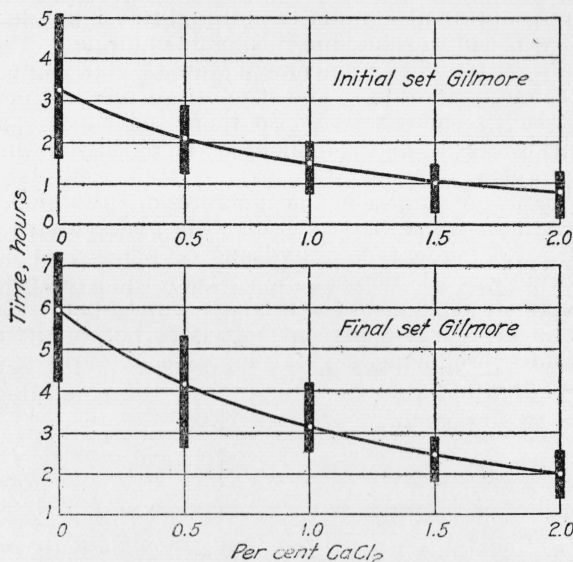


FIGURE 6.—Setting time of eight standard portland cements.

(2) *Strengths.*—A summary of the 1:3 standard sand mortar strengths is given in figure 7. This graph shows the strengths of the

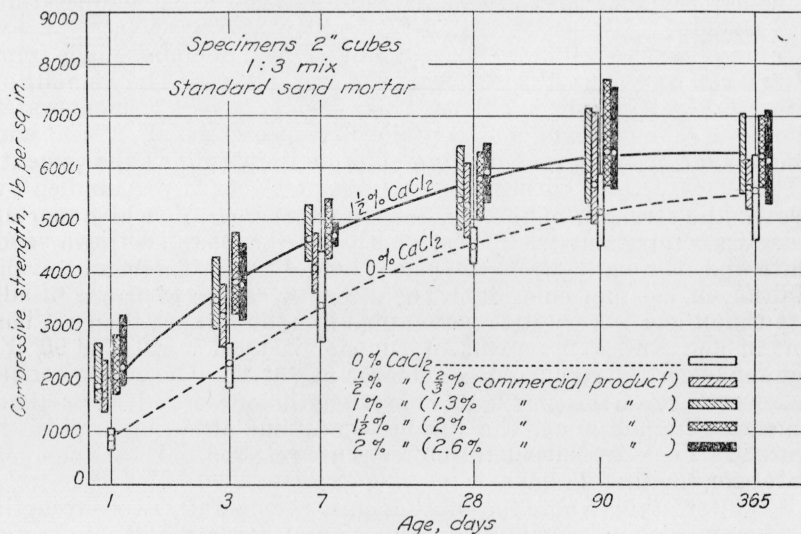


FIGURE 7.—Compressive strength of eight standard portland cements, 1:3 standard sand mortars.

8 standard portland cements with the addition of various percentages of calcium chloride. Not only were the early strengths of portland-cement mortar greatly increased by calcium chloride, but the 1-year

strengths were also increased. The results of the tests show that the mortar containing 1.5 percent of anhydrous (2 percent of commercial) calcium chloride has a strength approximately 15 percent greater than the plain mortar at 1 year; the strength at 1 day is practically doubled by the use of this amount of calcium chloride. The strengths of the mortars containing white cement were similarly affected by the addition of calcium chloride. The strength of the mortar made with high-early-strength cement was also increased by the addition of calcium chloride; the strengths in all cases being higher than those of the 8 standard cements.

The compressive strengths of the concretes of the standard cements are summarized in figure 8. At 1 day the average strength of the concrete with 1.5 percent of anhydrous (2 percent of commercial) calcium chloride was 128 percent higher than the average strength of the plain concrete, at 28 days the increase was 13 percent, at 90 days 9 percent, and at 1 year 8 percent. It is to be noted that calcium chloride, besides producing a great increase at early ages, also in-

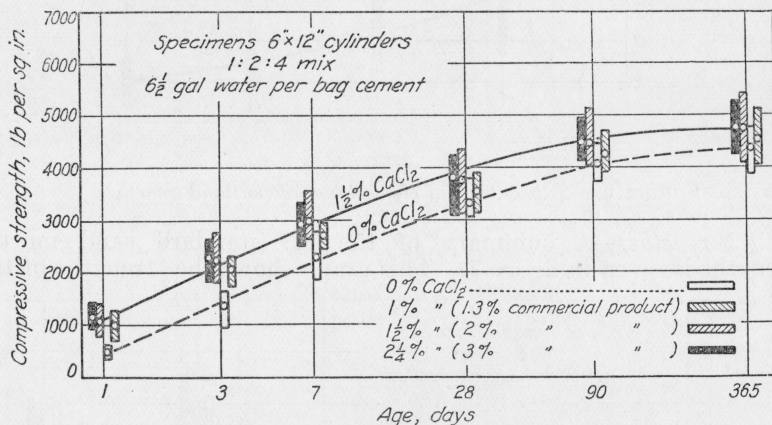


FIGURE 8.—Compressive strength of eight standard portland cements, 1:2:4 concrete.

creased the strength of the concretes up to 1 year, at which age the tests were terminated. The strengths of the concrete made with white and high-early-strength cement were likewise increased by the addition of calcium chloride. The strength curves of figure 8 indicate that there is very little advantage in adding more than 1.5 percent of anhydrous (2 percent of commercial) calcium chloride, the amount generally recommended for use at 70° F.

A summary of the plastic mortar strengths of 8 standard portland cements obtained under the various conditions of curing is given in figure 9. For convenience the storages are referred to by the temperatures for the first 28 days.

It is interesting to note the effect of curing temperatures on strengths of mortars without calcium chloride. The 1-day strength of the 40° F specimens is 475 lb/in.<sup>2</sup> (91 percent) less than that of the 70° F specimens, and the 40° F specimens require approximately 3 days to reach the 1-day strength of the 70° F specimens. At 28 days the 40° F specimens are approximately 1,000 lb/in.<sup>2</sup> (23 percent) lower



than the 70° F specimens. An increase in the storage temperature of 20 degrees, from 70 to 90° F, about doubles the 1-day strength. At both 28 and 90 days the strength of the 90° F specimens is less than the strength of the 70° F specimens.

The strengths of the mortars were increased for all percentages of calcium chloride added for the three storage conditions. At 1 day the strengths of the 40, 70, and 90° F specimens were increased 300, 145, and 90 percent, respectively, by the addition of 1.5 percent of anhydrous (2 percent of commercial) calcium chloride. At 3 days the percentage increases were 117, 68, and 41 for the respective curings. At 7 days calcium chloride increased the strengths of the specimens

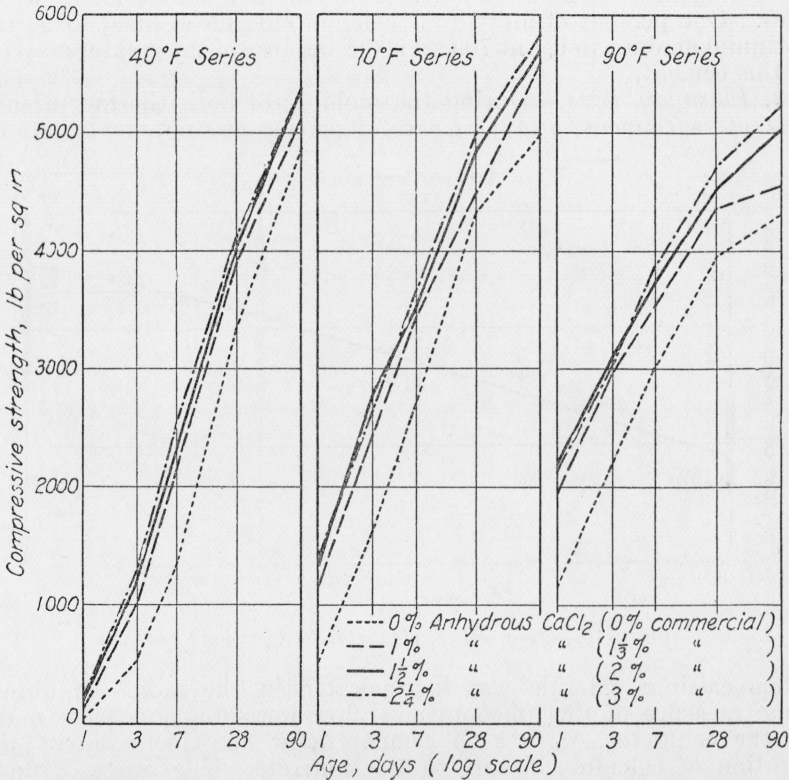


FIGURE 9.—Average plastic mortar strengths of eight standard portland cements.

cured at 40, 70, and 90° F, 75, 32, and 23 percent, respectively, but the 28-day strengths are increased only 20, 12, and 15 percent with the addition of 1.5 percent of calcium chloride. At 90 days the percentage increases were 10, 14, and 16 for the respective curings. Thus, it is seen that the greatest increase in strength due to the addition of calcium chloride is obtained at low temperatures and early ages.

It is interesting to note in figure 9, that the 1-day strengths of the specimens with no calcium chloride added, cured at 90° F, are approximately the same as those of the 70° F specimens containing 1.5 percent of anhydrous (2 percent of commercial) calcium chloride.

The increase in strength at 1 day, due to increasing the temperature from 70° to 90° F, is approximately the same as that produced at 70° F by the addition of 1.5 percent of calcium chloride. At 40° F the addition of 1.5 percent of calcium chloride produces approximately the same strength in 2 days that mortars without calcium chloride possess at 70° F in 1 day.

The strengths of the mortars containing white cement were within the same range as those containing standard cement, and the strengths were similarly affected by calcium chloride. Likewise, the strengths of the mortars containing high-early-strength cement were increased by the addition of calcium chloride for all storage conditions, but the strengths were higher than those of the standard cements at all ages. One percent of anhydrous calcium chloride seemed to be the optimum amount to use at 70 and 90° F because of the greater activity of this cement.

3. *Plasticity Tests.*—During the molding of both the mortar and concrete specimens, a greater ease of placing was noted when anhy-

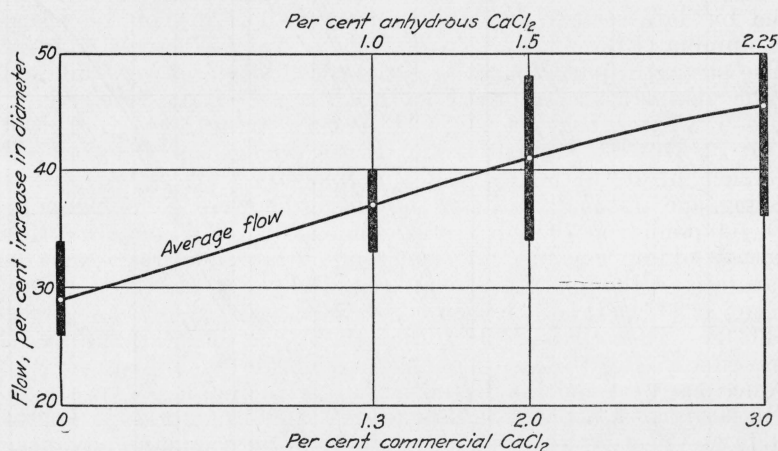


FIGURE 10.—Flow tests of eight standard portland cements.

drous calcium chloride was incorporated in the mix. To obtain some measure of this phenomenon, flow measurements were made on the concrete. With each cement flows were increased by the addition of calcium chloride to the concrete. The range of flows obtained on 8 standard cements as well as the average flow are plotted in figure 10 against the amount of calcium chloride added. The flow is expressed as the percentage increase in diameter after dropping the flow table 15 times, a distance of  $\frac{1}{8}$  inch.

Each point on the average flow curve represents the mean of 72 determinations. There was an increase in the average flow from 29 to 41 with the addition of 1.5 percent of anhydrous calcium chloride.

The flows of the concrete containing white cements were within the same range as the flows with standard cements, and the calcium chloride had approximately the same effect. The flow of the concrete containing high-early-strength cement was similarly increased by the addition of calcium chloride, but the flow was smaller in all

cases, being 16 with 0 percent and 21 with 1.5 percent of calcium chloride.

This increase in flow indicates increased workability. Thus, by adding calcium chloride less water may be used and a flow equal to that of plain concrete may still be obtained. Therefore, not only an increase in strength due directly to the addition of calcium chloride, but also a further increase in strength due to a decreased content of mixing water can be obtained.

## V. DISCUSSION AND RECOMMENDATIONS

A comparison of figures 8 and 9 shows that the plastic-mortar strengths at 70° F is sufficiently close to the concrete strengths to be comparable at the early ages. If at 40 and 90° F curing the plastic-mortar strengths are also comparable to the concrete strengths, the data of figure 9 clearly show the marked effect of curing temperature on the strength of the concrete. That the plastic-mortar strengths are comparable to the concrete strengths at 40° F is indicated by data secured by the Highway Laboratory of the District of Columbia (13).

The strength, particularly at early ages, decreases very markedly as the temperature approaches the freezing point. Referring to figure 9, we see that at 90° F the 1-day strength is 1,140 lb/in.<sup>2</sup>, at 70° F, 520 lb/in.<sup>2</sup>, while at 40° F the strength is 50 lb/in.<sup>2</sup> The difference in strength at these 3 temperatures decreased with increasing age until at 28 days the strengths were 4,000 pounds at 90, 4,400 pounds at 70, and 3,300 pounds at 40° F. The proportional effect of adding calcium chloride is much larger at the lower temperatures. Although the strength at 3 days is increased only 28 percent at 90° F, it is increased 60 percent at 70° F, and 115 percent at 40° F. Thus, it is evident that the lower the temperature, the more effective is the use of calcium chloride as an admixture to produce early strength. Referring again to figure 9, we see that up to 90 days, 2 percent of commercial calcium chloride is approximately as effective as 3 percent. There is no economic advantage, then, in using more than 2 percent integrally in the concrete.

There is an added advantage in using calcium chloride in cold weather in the increased rapidity with which it causes the development of heat. Construction at low temperature requires special measures to assure a rate of hydration of the cement that will develop early strengths. In thin concrete slabs, where the heat may be readily dissipated, this increased rapidity of heat development will compensate for some of the heat lost and will decrease the curing time and the time necessary for the use of coverings, or other means of maintaining a satisfactory temperature for hydration (11, 12).

Figure 11 has been prepared to show the length of time that will be required for representative standard and high-early-strength cements, both with and without calcium chloride, at placing and curing temperatures of 40, 70, and 90° F, to obtain a strength of 2,500 lb/in.<sup>2</sup>. It will be noted from the data (fig. 11) that the amounts of calcium chloride added to the cements at the higher temperatures were less than at the lower temperature. Several factors contributed to the choice of the amounts used.

Lerch and Bogue (3), in a study of the heat of hydration of portland-cement paste, found that higher initial temperatures accelerate the reactions of hydration and increase the quantity of heat liberated from the cements at early ages. Figure 12, which gives a typical graph of the effect of initial temperature on the heat of

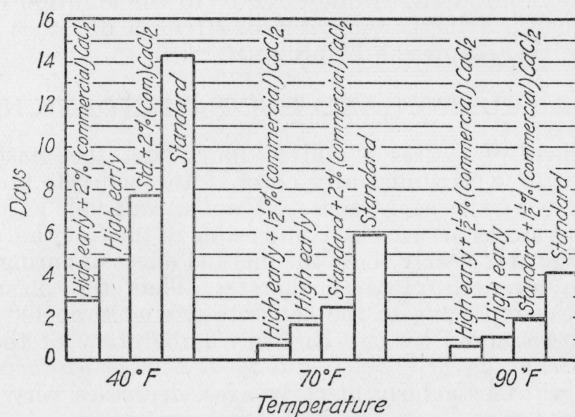


FIGURE 11.—Effect of curing temperature and addition of calcium chloride on length of time required for concrete to attain 2,500 lb/in.<sup>2</sup> strength (based on plastic mortar strength).

hydration, shows that as the initial temperature is increased the maximum temperature attained is increased, and the time required to reach the maximum temperature is decreased.

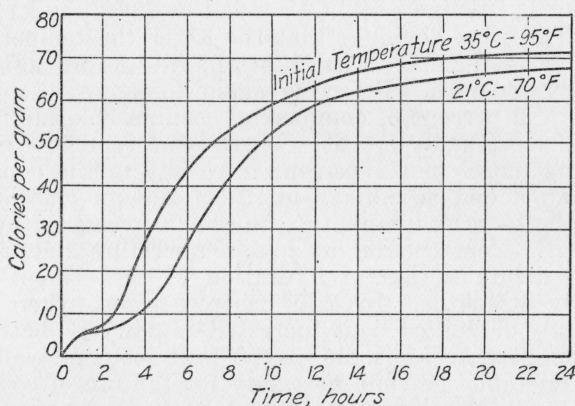


FIGURE 12.—Typical curves showing the effect of initial temperature on the rate of evolution of heat from portland cement.

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Added to this accelerating effect of the higher temperatures is the accelerating action of calcium chloride which, according to a comparison of heat tests previously mentioned and figure 12, is of equal importance to the acceleration caused by raising the temperature from 70 to 95° F. Therefore, when calcium chloride is



added to cement at a higher temperature, two accelerating actions, which are additive, are superimposed. Several investigators (2, 3, and 14) have shown that there is a direct relation between the rate of evolution of heat, or temperature rise, and the rate of hardening or set. Too great an increase in either, or both, of the accelerating factors, therefore, is likely to cause a time of set so rapid that finishing of the placed concrete would be difficult.

An initial stiffening of the mix occurred at 90° F during the mixing and molding of the plastic-mortar specimens when as much as 3 percent of commercial calcium chloride was added. This made the finishing of some of the specimens difficult. Although with 2 percent of calcium chloride no stiffening was noted, the workability of the mortar, when molded at 90° F, appeared to be at its maximum with only 1.5 percent of commercial calcium chloride present. Mortar with less admixture was less workable.

The recommended amount to be added to the standard and white portland cements at 40 and 70° F was found to be 2 percent of commercial calcium chloride; at 90° F the amount should be decreased to 1.5 percent. Since it has been shown that the accelerating action of both increased initial temperature and calcium chloride is greater for the high-early-strength cement, not more than 1.5 percent of commercial calcium chloride is recommended for high-early-strength cement at either 70 or 90° F (15).

## VI. SUMMARY

The following conclusions have been drawn from the investigation:

1. The heat contributed by the 4 major compounds of portland cement during the first 24 hours was determined on neat cement pastes and also with the pastes to which 1 percent of anhydrous calcium chloride was added. Factors are given from which the heat evolved in 24 hours by a portland cement may be computed from its compound composition, either with no calcium chloride or when 1 percent of anhydrous calcium chloride is present. The addition of calcium chloride increased the heat contributed by dicalcium silicate and tetracalcium alumino-ferrite, decreased the heat from tricalcium aluminate, and had little or no effect on the heat contributed by tricalcium silicate.

2. The addition of calcium chloride increased the heat evolved by each of the cements tested up to 24 hours, even though that part of the total heat developed by the tricalcium aluminate was decreased. Although there was not much change in the total heat evolved in 24 hours, the addition of calcium chloride markedly increased the rapidity with which this heat was evolved.

3. Sixty experimental portland cements were grouped according to the amount of heat evolved during the first 24 hours of hydration. It was found that for the group that developed only 30 to 40 calories per gram, the addition of 1 percent of anhydrous calcium chloride increased the heat 7 calories per gram. Groups which evolve greater amounts of heat liberate less and less heat with the addition of calcium chloride, until in that group liberating from 70 to 80 calories per gram the addition of calcium chloride lowers the amount of heat liberated by 2 calories per gram.

4. The study (at 70° F) of the mortar strengths of 60 experimental portland cements of widely varying composition at ages up to 28 days, beyond which no measurements were made, shows:

(a) Corroborating the findings of other investigators, the compound composition of portland cement greatly influences its strength. The strength contributed by each of the four major components has been computed.

(b) Calcium chloride increased the strengths of cement mortars, especially marked when the composition of the cement was within the range encountered in commercial portland cements.

(c) The addition of calcium chloride increased the strength contributed by dicalcium and tricalcium silicates.

(d) The addition of calcium chloride increased the strength contributed by tricalcium aluminate for the first few days, but after this time decreased the strength contributed by this compound.

(e) The contribution of tetracalcium aluminoferrite to the strength is small. The addition of calcium chloride appears to make this factor slightly negative at all ages.

5. The tests of 8 standard, 2 white and 1 high-early-strength commercial portland cements, selected to obtain large variations in composition, show:

(a) The setting times of cement at 70° F were decreased by the addition of increasing amounts of calcium chloride.

(b) The addition of calcium chloride increased the strength of each of the cements at all ages up to 1 year, beyond which tests were not made. Not only were the early strengths greatly increased by the addition of calcium chloride, but the 1-year strengths were appreciably increased. Tests at 40 and 90° F also showed an increased strength at all ages up to 90 days, at which time the tests were terminated.

(c) At 70° F the flow or workability of the concrete was increased by the addition of calcium chloride up to and including 3 percent of commercial calcium chloride.

(d) Tests at 40, 70, and 90° F showed that the lower the initial curing temperatures the more effective is the use of calcium chloride as an admixture in increasing the early strength.

(e) Integral use of calcium chloride was effective in accelerating the curing of all the cements. It is, therefore, of value in cold-weather construction in decreasing the time necessary for protecting the concrete.

6. A tabulation is given showing the time required for normal portland and high-early-strength portland cements to attain a compressive strength of 2,500 lb/in.<sup>2</sup> The effects of different curing temperatures, both with and without calcium chloride, are given. The optimum amount of calcium chloride which should be used at the three curing temperatures studied, was found to be:

Temperatures	Commercial calcium chloride	Type of cement
°F	Percent	
40	2	All cements. Normal and white. High early. All cements.
70	2	
90	1.5	
	1.5	

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