PROGRESS REPORT ON THE REACTION OF CALCIUM CHLORIDE ON PORTLAND CEMENT[1]

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SYNOPSIS

The addition of calcium chloride appears to increase somewhat the heat contributed at the end of 24 hours by dicalcium silicate and tetracalcium ferro-aluminate and to decrease the heat from tricalcium aluminate present in cements The heat contributed by tricalcium silicate shows very little change when calcium chloride is added Calcium chloride increases the rate at which the heat is evolved from all cements tested and in general gives an increase of about four calories per gram of cement at 24 hours It decreased the time of set of the 11 commercial cements and increased the flow of the concrete mix and the strength of the resulting concrete at all ages to 90 days, beyond which results have not yet been obtained

INTRODUCTION

The Calcium Chloride Association has maintained a fellowship at the Bureau of Standards to study the reactions of calcium chloride with cements and their constituents and to obtain more information on the effect of this material on concrete made from present day cements The results of the complete investigation of the effects of calcium chloride on cements and concrete cannot be given at this time since the long-time tests have not been completed However, it is felt that certain salient factors are of sufficient interest to those concerned with the use of calcium chloride in concrete to warrant a brief paper at this time on some of the results obtained Therefore the data herewith presented relate to the short-time tests and include the effect of calcium chloride on the heat of hydration, setting time, strength and consistency of a selected group of cements

It is planned to publish that phase of the study dealing with the physico-chemical reactions between calcium chloride and the constituents of cement as a separate paper

DESCRIPTION OF THE CEMENTS AND CALCIUM CHLORIDE

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

[1] Publication Approved by the Director of the Bureau of Standards of the U S Department of Commerce

Sixty experimental cements of varying composition were furnished by the Portland Cement Association Fellowship at the Bureau of Standards for certain heat studies herein reported

The calcium chloride used was a commercial flaked hydrated product containing 77 1 per cent $CaCl_2$ and the amounts added to the cements are reported as percentage $CaCl_2$ by weight of cement.

EFFECT OF CALCIUM CHLORIDE ON HEAT EVOLVED DURING FIRST TWENTY-FOUR HOURS OF HYDRATION

General Consideration. It has long been recognized that certain reactions which take place during the setting and hardening of cements result in an evolution of heat. During the past few years there has been an added interest in the quantity of this heat evolved as it relates to the properties of the concrete. It seemed advisable, therefore, to determine the effect of the addition of calcium chloride upon the heat developed as cement hydrates

From measurements of the temperature rise of a given mixture of cement and water during the first twenty-four hours the quantity of heat evolved during this period can be calculated This method also gives the rate at which the heat is evolved

Heat of Hydration of Sixty Special Cements The sixty samples of laboratory cements above referred to 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 per cent anhydrous calcium chloride) could be made.

The apparatus used for measuring directly the heat of hydration was that developed at the 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 mixing device Copper-constantin thermocouples were inserted into the mixture and the can placed in a double-walled vacuum flask which was in turn tightly closed and placed in an air thermostat maintained at 21 ±1°C. The apparatus was so arranged that eight separate determinations could be made simultaneously

From the data obtained in this manner it was possible to calculate the heat evolved by the cement at any given period[3] after making the necessary correction for the radiation loss of the vacuum flask and its contents

The contributions of the individual compounds to the heat of hardening were calculated by the method of least squares after computing the

[2] Variations in Standard Portland Cements, P H Bates, Jour Amer Concrete Institute, Vol 1, page 65, Nov 1929

[3] The Heat of Hydration of Portland Cement Paste, Lerch and Bogue, Bureau of Standards Jour of Research (RP684) Vol 12, pp 645–664, May, 1934

percentages of the compounds in the cements by the method of Bogue[4] and assuming that a linear relationship exists between the compound composition of the cement and the heat evolved The values obtained from these cements (Table I) show the same trends as those reported by Blank[5] and by Wood and his co-workers,[6] namely that tricalcium aluminate 3CaO Al_2O_3, gives the greatest heat evolved (expressed in calories

TABLE I

CONTRIBUTION OF INDIVIDUAL COMPOUNDS TO HEAT OF HARDENING
(In calories of each per cent in one gram of cement)

Compound	Value for 0% $CaCl_2$ at 1 Day	Probable Error	Value for 1% $CaCl_2$ at 1 Day	Probable Error	Blank's Value at 1 Day	Wood s Value at 3 Days
Tricalcium Silicate	80	± 02	78	± 02	57	98
Beta Dicalcium Silicate	19	± 02	26	± 02	095	195
Tricalcium Aluminate	1 62	± 07	1 47	± 06	2 00	1 70
Tetracalcium Ferro-Aluminate	01	± 08	25	± 06	19	29

TABLE II

CHANGES IN THE TOTAL HEAT EVOLVED AT TWENTY-FOUR HOURS BY ADDITION OF ONE PER CENT OF CALCIUM CHLORIDE TO EXPERIMENTAL CEMENTS

Grouping—Heat Evolved 24 Hours No $CaCl_2$	No of Cements in each Group	Average Changes Produced by 1% $CaCl_2$	Average Compound Compositions			
			$C_3A^{(1)}$	$C_4AF^{(2)}$	$C_2S^{(3)}$	$C_3S^{(4)}$
(Calories per g)		*(Calories per g)*	%	%	%	%
30–39 9	9	+7	3	15	47	30
40–49 9	12	+5	4	14	35	42
50–59 9	24	+4	10	12	34	42
60–69 9	16	0	10	11	25	52
70–79 9	3	−2	15	7	21	53

(1) C_3A = 3CaO Al_2O_3.
(2) C_4AF = 4CaO Al_2O_3 Fe_2O_3.
(3) C_2S = 2CaO SiO_2 (Beta)
(4) C_3S = 3CaO SiO_2.

for each per cent present in each gram of cement) tricalcium silicate, 3CaO SiO_2, being next in order The addition of calcium chloride appears to increase somewhat the heat contributed by dicalcium silicate, 2CaO SiO_2 and tetracalcium ferro-aluminate, 4CaO Al_2O_3 Fe_2O_3 and to decrease the heat from tricalcium aluminate The heat contributed

[4] Calculations of the Compounds in Portland Cement, R. H Bogue, Ind & Eng Chem , Anal Ed 1, page 192, 1929

[5] Comparison of Selected Portland Cements in Mass Concrete Tests, Robert T Blank, J Am Concrete Inst , Vol 5 (No 1), page 9, 1933

[6] Effect of Composition of Portland Cement on Heat Evolved During Hardening Wood, Steinam and Starke Ind Eng Chem , Vol 4, p 1207 (1930)

by tricalcium silicate shows very little change when calcium chloride is added

In Table II the experimental cements are divided into five groups on the basis of the calories evolved per gram of cement at the end of twenty-four hours without addition of calcium chloride Column 1 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 one per cent calcium chloride and the remaining four columns the average compound composition From this table it can be seen for the experimental cements that an increase in the calories of heat evolved from group to group was accompanied by an increase in percentage of both the tricalcium aluminate and tricalcium silicate, the two compounds as shown from Table I to be those contributing the greater quantities of heat of hydration Furthermore, the increase in the heat evolved because of the addition of one per cent calcium chloride is greatest in the first group (cements of lowest heat), becomes less in the succeeding groups, reaching zero for the fourth group, and in the fifth group there is an actual decrease of two calories 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 I that each per cent of tricalcium silicate present in one gram of cement evolves the same number of calories with and without calcium chloride The changes do, however, appear to be inversely related to the amounts of tricalcium aluminate and directly to those of dicalcium silicates and tetracalcium ferro-aluminates present in each group and in this respect are in agreement with the data of Table I

Heat of Hydration of Eleven Commercial Cements The heat evolved from eleven commercial cements during the first 24 hours of hydration was measured with and without calcium chloride to determine the nature of the change produced by the addition of 0 5, 1, 1 5 and 2 per cent of anhydrous calcium chloride

The heat data pertaining to these commercial cements were analyzed in the same manner as described for the experimental cements and similar conclusions were obtained as to the contribution of heat by the individual compounds present as well as to the effect of calcium chloride

The effect of the addition of calcium chloride on the heat curves for cement B (Standard portland) is shown in Figure 1 As the amount of calcium chloride is increased the rate of heat evolution is increased The addition of 1 5 per cent of anhydrous calcium chloride though increases this rate proportionately more than two per cent The amount of heat developed at 24 hours does not change more than a few calories for the various percentages of calcium chloride added The other seven standard and the two white cements behave in a similar manner upon the addition of calcium chloride

Time-temperature curves plotted from the temperature data pertaining to these cements show that calcium chloride generally increases the rate of temperature rise and decreases the time to reach the maximum temperature However, with the high-early strength cement the maximum temperature attained both with and without calcium chloride was at or near the boiling point of water so that the heat of hydration could not be ascertained satisfactorily since an undetermined portion of the heat was involved in the latent heat of vaporization of water.

EFFECT OF CALCIUM CHLORIDE ON THE PHYSICAL PROPERTIES OF MORTARS AND CONCRETES

In order to obtain a measure of the effect of calcium chloride on the physical properties of the cements in mortars and concretes it was deemed advisable to control all factors, as far as possible, so that the admixture of calcium chloride would be the main variable

Making the Test Specimens The usual evaluation tests for portland

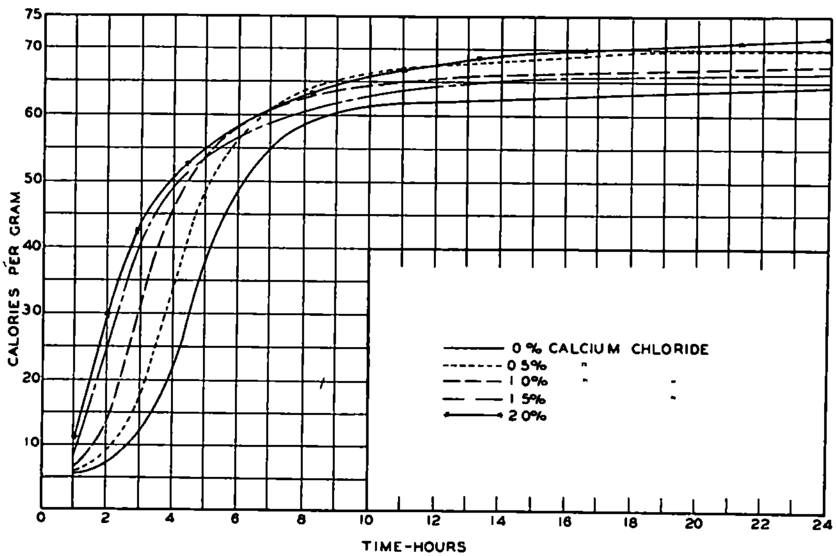

Figure 1. Heat Curves for Cement B

cement[7] were made except that two inch mortar cubes were substituted for the briquets In these tests 0, 0 5, 1, 1 5 and 2 per cent anhydrous calcium chloride, respectively, were added to the gauging water. The mortar specimens were kept in the molds 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 x 12 inch cylinders made from a 1:2:4 mix by volume, using local sand and gravel The amount of

[7] Federal Specification SS-C-191 for Cement, Portland; Standard Methods of Sampling and Testing Portland Cement Am Soc Testing Materials, C77-32

water (6 5 gallons per sack) used for gauging gave a cement-water ratio of 1 73 by weight and contained, respectively 0, 1, 1 5 and 2 25 per cent of anhydrous calcium chloride by weight of the cement

The effect of two curing temperatures during the first 24 hours was studied by means of plastic mortar tests [8] Pit run Ottawa sand was used as the aggregate The same cement-water ratio and percentages of admixtures of calcium chloride were used as in the concrete tests One group of specimens was made and stored at 70°F until tested Another group was molded at 90°F and stored at that temperature for the first 24 hours The specimens were then removed from the molds and placed in water at 70°F.

Results The times of set are shown in Figure 2 It will be noted

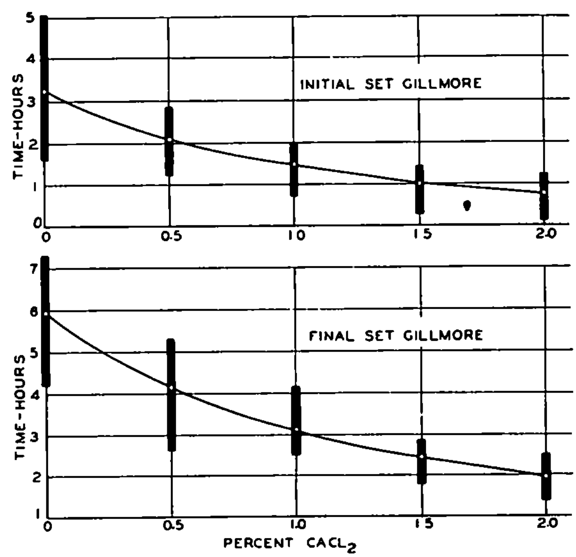

Figure 2 Setting Time of Standard Portland Cements

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 Similarly the addition of calcium chloride to the white and high-early strength cements, not given in Figure 2, shows the same effect as obseved with the standard cements All pats, both with and without calcium chloride, were sound

A summary of the concrete strengths obtained on eight standard cements is given in Figure 3 The concretes with all percentages of calcium chloride show increased strength over the plain concrete at all ages tested At one day the average strength of the concrete with 1 5 per cent admixture was 123 per cent higher than the average strength of

[8] A Plastic Mortar Compression Test for Cement E M. Brickett, Am Soc Testing Mats Vol 28, (Part II) page 43, 1928

the plain concrete. At 28 days the increase was 13 per cent and at 90 days 9 per cent, indicating that calcium chloride has a greater accelerating action at early ages Figure 3 indicates that there is very little advantage of adding more than two per cent commercial (1 5 per cent anhydrous) calcium chloride, the amount generally recommended for use at 70°F. The strength of the concrete containing white cement was within the same range as for those with standard cements and calcium chloride had apparently the same effect thereon The strength of the concrete made with high early strength cement was also increased by the addition of calcium chloride However, the strengths were higher than those of the eight standard cements in all cases

The effects of the addition of calcium chloride on the strengths of the

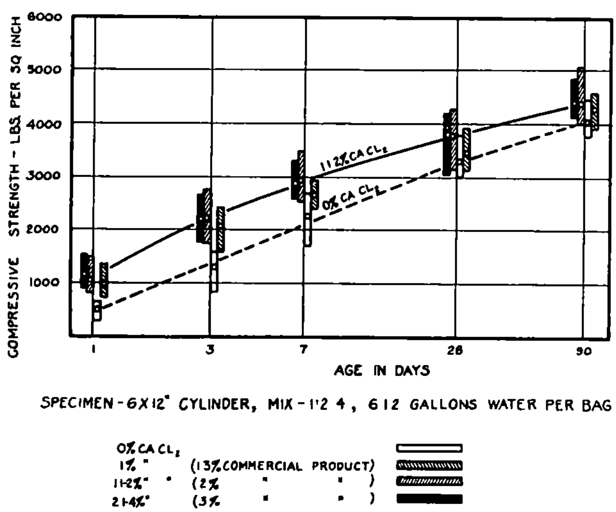

Figure 3. Concrete Strength Summary of Eight Standard Portland Cements

cements when tested in 1:3 standard sand mortars showed the same trends as observed on the concrete strengths

The tests of the strength at different curing temperatures have been undertaken to ascertain how strength of concrete may be affected by the addition of calcium chloride under the temperature conditions encountered during the construction season Specimens have been made for two curing temperatures (70 and 90°F) and curing a group of specimens at a temperature of 40°F is being studied Since this part of the investigation is not finished a tabulation of the results obtained to date will not be included in this report It is of interest, however, to note here that the one day specimens without calcium chloride cured at 90°F. have approximately the same strength as the 70°F specimens containing calcium chloride

During the molding of both the mortar and concrete specimens a greater ease of placing was noted when 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 additions of calcium chloride to the concrete The range of flows obtained on eight standard cements as well as the average flow are plotted in Figure 4 against the amount of calcium chloride added The flow is expressed as the per cent increase in diameter after dropping the flow table 15 times, a distance of ⅛ 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 per cent anhydrous calcium chloride. The increase in flow was more marked in the range of 0 to 1 5 per cent calcium chloride than beyond 1 5 per cent.

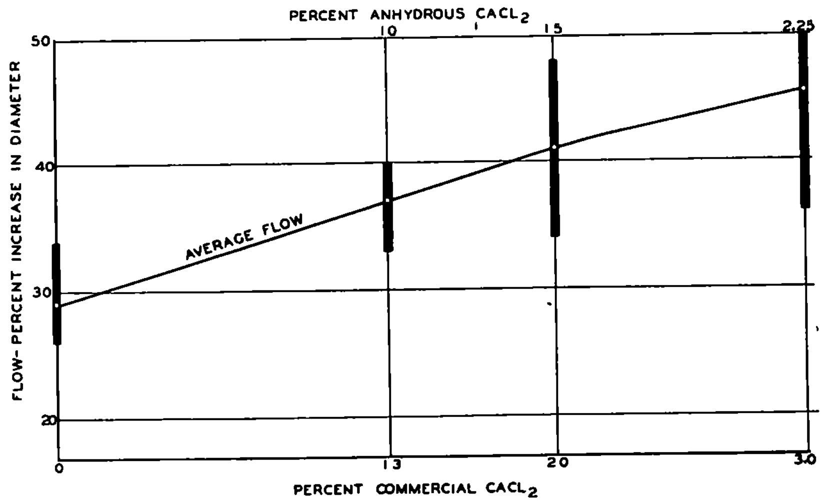

Figure 4 Flow Tests of the Concrete of Eight Standard Portland Cements Mix—1 2.4. 6 5 gallons water per bag

The flows of the concrete containing white cement were within the same range as for those with standard cement, 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 per cent and 21 with 1 5 per cent calcium chloride.

SUMMARY

In considering the results obtained in this investigation, it should be borne in mind that the tests are by no means finished, and that later information may alter some of the following tentative conclusions

1 Calcium chloride increases the rate of heat evolution of all cements included in the investigation

2 Calcium chloride increases the total heat of hydration of low heat

cements and may decrease the heat of hydration of high heat cements at 24 hours

3 The chemical composition of the cement has an important effect upon both the rate and total amount of heat of hydration developed during the first 24 hours The general effect of calcium chloride over the range in compositions studied was a tendency to level the heat of hydration to an average increase of about four calories per gram at 24 hours

4 The times of set of 11 commercial cements were decreased by adding increasing amounts of calcium chloride The greatest proportional decrease was obtained by the addition of two per cent commercial calcium chloride

5 Additions of calcium chloride did not affect the soundness of the cements

6 The addition of calcium chloride increased the strength of the concrete made from the cements tested at all ages to 90 days, beyond which results have not yet been obtained

7 The flow of concrete was increased by the addition of calcium chloride

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