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EFFECT OF GLASS CONTENT UPON THE HEAT OF HYDRATION OF PORTLAND CEMENT

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ABSTRACT

The heat of hydration was determined, by the heat-of-solution method, for a number of portland cements prepared from clinker which had been subjected to various heat treatments to produce different glass contents. The results indicate that, when different cements are ground to about the same degree of fineness, the quantity of heat evolved between 7 and 28 days will be dependent on a number of factors, two of the most important of which are: (1) The composition of the cement, and (2) the glass content of the clinker. The glass content not only influences the heat of hydration directly, but also influences it indirectly, through its effect upon the true compound composition. No consistent relation was observed between the glass content and the quantity of heat evolved at 3 days. At 7 and 28 days the quantity of heat evolved for any given composition increased consistently with increasing glass contents. Sone reasons are advanced to explain why the difference in glass content, together with the changed compound composition resulting therefrom, may affect the heat of hydration of the cement at various ages.

CONTENTS

I. INTRODUCTION

Studies of the heat of hydration of portland cement have been extended to include an investigation of the effect of the glass content of the clinker on the heat liberated during the hardening of the cement. The present investigation includes a study of 21 samples of standard portland cement clinker as obtained from different plants throughout the United States and one additional sample of sulfate-resistant cement clinker. It also includes a study of these clinker compositions after they were subjected to special heat treatments in the laboratory. These treatments were of such character that different degrees of crystallization of the clinker compounds and consequently different glass contents might be anticipated. The approximate glass content of each clinker, as determined by the heat-of-solution method, has been given in a previous report [1].[2]

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[2] Numbers in brackets indicate the literature references at the end of this paper.

II. EXPERIMENTAL PROCEDURE

1. TREATMENT OF THE CLINKER

In the request to the plants which supplied the clinker, it was suggested that the clinker should be freshly burned, should not be water-quenched, and should not have been exposed to undue moisture on the stock pile. As a result of this request the samples, as received from the plants, were all of relatively low ignition loss.

Each clinker sample, as received, was crushed between rolls, thoroughly mixed, and divided into three lots; one lot to be used as received, one lot to be reburned and rapidly cooled, and one lot to be reburned and slowly cooled. These samples were prepared and reburned in laboratory kilns by W. C. Taylor, following methods described in previous reports [2, 3]. The clinker to be rapidly cooled was reburned in an experimental rotary kiln at 1,400° C. The clinker obtained from this kiln was small, not exceeding 0.5 inch in diameter, and in the normal operation of the kiln the clinker cooled from the clinkering temperature to about 1,000° C, in 2 or 3 minutes. This clinker was designated "rapidly cooled clinker" and is identified by *Q* in the tables.

The clinker to be slowly cooled was placed in an updraft gas-fired kiln and heated to 1,400° C. The gas and air were then adjusted in such manner as to allow the temperature of the clinker to decrease slowly over a 2-hour period to 1,250° C. The gas and air were then cut off and the clinker was allowed to cool with the kiln. This clinker was designated "slowly cooled clinker," *S*. The third lot of clinker was used as received from the plant and was designated "plant clinker," *P*.

These various samples of clinker showed large differences in their approximate glass content as determined by the heat-of-solution method [1]. For any given composition the glass content was highest (9 to 22 percent) in the rapidly cooled clinker and lowest (0 to 3 percent) in the slowly cooled clinker. In some instances the glass content of the plant clinker as received was of the same order as that of the slowly cooled clinker. In other cases the glass content of the plant clinker closely approached the glass content of the rapidly cooled clinker.

2. PREPARATION OF THE CEMENT

Gypsum was added to the clinker in such quantity that the resulting cements would contain 1.8 percent of SO_3 by weight, and the cements were then ground to about the same fineness. The specific surface, by the Wagner [4] turbidimeter, ranged from 1,540 to 1,840 and averaged 1,690 cm^2/g. The grinding of the cements was performed at the research laboratory of the Portland Cement Association, in Chicago.

3. PREPARATION AND CURING OF THE PASTES

Neat cement pastes were prepared for the determination of the heat of hydration. Two hundred grams of cement and 80 g of water were mixed together and stirred vigorously with a mechanical stirrer. The paste was then placed in glass vials and the vials tightly stoppered and sealed with paraffin wax. The vials were stored in a vertical position at 70° F for 1 day and at 100° F thereafter, until the time of test.

TABLE 1.—*Heat of hydration analysis, calculated composition and approximate glass content of commercial portland cement clinker and the glass contents of the same clinker after being subjected to special heat treatments*

Clinker [1]		Chemical composition [2]									Major constituents, corrected					Additional minor constituents				Calculated compound composition						Al_2O_3/Fe_2O_3 ratio	Approximate glass content	Specific surface Wagner turbidimeter (sq cm/g)	Water for normal consistency (percent by weight)	Heat of hydration, neat cement (cal/g)			Clinker [1]
		SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Loss on ignition	Insoluble residue	Free CaO	SiO_2	Fe_2O_3 less FeO as Fe_2O_3	Al_2O_3 less TiO_2	CaO less free CaO	MgO	FeO	TiO_2	Na_2O	K_2O	C_3S	C_2S	C_3A	C_4AF	MgO	Free CaO					3 days	7 days	28 days	
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%		%				
1S	13721	21.5	2.2	6.3	64.3	3.0	0.7	0.4	0.2	0.4	21.5	2.2	6.0	63.1	3.0	0	0.3	0.1	1.6	50.0	24.0	12.2	6.7	3.0	1.2	2.9	0	1640	24.0	88	90	94	1S
1P	13722									1.2																	2	1746	24.0	85	88	94	1P
1Q	13723									1.5																	8	1540	21.5	88	92	97	1Q
2S	13724	20.6	5.7	6.0	64.1	1.8	.6	.2	.2	0.1	20.6	5.5	5.6	63.3	1.8	.2	.4	.3	0.7	55.5	17.2	5.6	16.7	1.8	0.8	1.1	1	1660	21.5	70	74	82	2S
2P	13725									.8																	5	1640	21.5	66	73	81	2P
2Q	13726									.9																	21	1560	21.0	69	82	89	2Q
3S	13727	22.4	2.7	5.9	63.9	4.0	.1	.3	.2	.2	22.4	2.3	5.4	63.5	4.0	.4	.5	.6	.2	48.5	27.7	10.4	7.0	4.0	0.4	2.2	0	1650	24.5	62	75	90	3S
3P	13728									.4																	11	1580	22.5	72	79	97	3P
3Q	13729									.4																	16	1660	22.0	74	84	105	3Q
4S	13730	19.8	7.0	5.1	62.7	4.2	.1	.2	.4	.3	19.8	5.3	4.7	58.5	4.2	1.5	.4	.5	.2	48.3	20.3	3.5	16.1	4.2	4.2	0.8	1	1740	21.5	60	66	73	4S
4P	13731									4.2																	21	1800	22.0	62	66	77	4P
4Q	13732									1.6																	22	1700	21.5	62	73	80	4Q
6S	13736	21.7	3.1	6.2	66.6	1.4	.3	.2	.2	0	21.7	3.1	5.9	66.2	1.4	0	.3	.1	.1	60.5	16.7	10.4	9.4	1.4	0.4	2.0	3	1680	23.0	72	91	96	6S
6P	13737									.4																	2	1820	22.5	74	92	99	6P
6Q	13738									.5																	14	1720	22.5	69	93	106	6Q
7S	13739	21.1	2.4	7.2	64.2	3.4	.4	.2	.2	tr	21.1	2.4	6.9	63.8	3.4	tr	.3	.4	.6	49.6	23.1	14.2	7.3	3.4	.4	3.0	2	1680	26.0	79	93	99	7S
7P	13740									0.4																	8	1660	23.5	78	94	98	7P
7Q	13741									.6																	21	1660	23.0	81	100	107	7Q
8S	13742	22.5	3.0	5.3	64.5	3.5	.3	.3	.1	.1	22.5	3.0	4.9	63.9	3.5	0	.4	.2	.5	51.9	25.4	8.0	9.1	3.5	.6	1.8	0	1660	23.5	72	95	96	8S
8P	13743									.6																	11	1670	21.5	70	97	100	8P
8Q	13744									.8																	12	1660	21.5	69	99	112	8Q
9S	13745	22.7	2.2	5.9	63.6	4.2	.3	.3	.3	.1	22.7	2.2	5.6	62.8	4.2	0	.3	.4	.5	42.3	33.1	11.1	6.7	4.2	.8	2.7	0	1640	25.5	67	89	93	9S
9P	13746									.8																	8	1630	22.5	66	91	97	9P
9Q	13747									.9																	14	1640	22.5	68	97	102	9Q
10S	13748	23.5	2.9	5.1	65.0	1.3	.6	.5	.2	.2	23.5	2.9	4.8	62.9	1.3	0	.3	.3	.8	41.0	36.5	7.8	8.8	1.3	2.1	1.8	1	1780	23.5	69	73	84	10S
10P	13749									2.1																	2	1660	23.5	67	75	86	10P
10Q	13750									2.0																	10	1680	22.5	66	78	90	10Q
11S	13751	22.0	5.1	4.9	66.3	0.8	.1	.2	.2	0.1	22.0	5.1	4.6	66.1	0.8	0	.3	.7	.2	63.7	15.0	3.6	15.5	0.8	0.2	1.0	3	1760	22.5	70	82	89	11S
11P	13752									.2																	7	1740	22.0	68	80	95	11P
11Q	13753									.3																	8	1610	22.0	63	78	99	11Q
12S	13754	22.0	6.2	5.2	63.1	2.4	.2	.3	.3	0	22.0	6.2	4.9	63.1	2.4	tr	.3	.3	.4	47.9	27.0	2.5	18.9	2.4	tr	0.8	1	1760	22.5	65	74	84	12S
12P	13755									tr																	9	1710	22.5	64	75	89	12P
12Q	13756									0.1																	21	1590	21.5	65	79	93	12Q
13S	13757	21.9	2.7	5.8	64.1	4.3	.4	.2	.2	.1	21.9	2.7	5.4	63.7	4.3	0	.4	.2	.6	52.7	23.1	9.8	8.2	4.3	0.4	2.1	0	1710	24.0	74	91	98	13S
13P	13758									.4																	4	1610	22.5	74	96	99	13P
13Q	13759									.6																	15	1630	22.0	70	95	102	13Q
14S	13760	21.9	2.5	5.3	64.2	3.9	.5	.4	.3	tr	21.9	2.5	5.0	63.3	3.9	0	.3	.3	1.0	54.0	22.0	9.1	7.6	3.9	.9	2.1	0	1780	24.5	77	85	91	14S
14P	13761									0.9																	6	1700	23.0	74	83	93	14P
14Q	13762									.8																	15	1770	22.0	74	91	101	14Q
15S	13763	21.8	3.0	5.7	63.4	4.2	.6	.3	.1	.1	21.8	3.0	5.4	62.1	4.2	0	.3	.3	0.9	46.6	27.4	9.2	9.1	4.2	1.3	1.9	2	1780	25.0	85	87	92	15S
15P	13764									1.3																	5	1630	23.5	80	86	93	15P
15Q	13765									1.4																	16	1800	23.0	77	89	100	15Q
16S	13766	22.3	2.6	6.3	65.0	3.3	.2	.2	.2	0	22.3	2.2	6.0	64.6	3.3	.4	.3	.2	.4	50.0	26.3	12.2	6.7	3.3	0.4	2.4	0	1840	26.5	79	90	96	16S
16P	13767									.4																	11	1740	23.5	71	90	98	16P
16Q	13768									.3																	17	1740	23.0	74	95	107	16Q
17S	13769	23.0	2.6	6.2	66.9	1.3	tr	.2	.2	.2	23.0	2.6	5.8	66.5	1.3	0	.4	.1	.2	53.3	25.7	11.0	7.9	1.3	.4	2.4	0	1840	25.0	71	85	95	17S
17P	13770									.4																	5	1660	23.0	--------	85	97	17P
17Q	13771									.5																	12	1740	22.0	77	90	100	17Q
18S	13772	21.7	2.7	6.1	64.4	3.6	0.3	.2	.1	.1	21.7	2.1	5.8	63.6	3.6	.5	.4	.2	.8	62.0	23.0	11.8	6.4	3.6	.8	2.3	0	1720	25.5	79	86	96	18S
18P	13773									.8																	10	1680	24.0	80	87	98	18P
18Q	13774									.5																	18	1760	23.0	79	88	103	18Q
19S	13775	22.1	2.8	5.5	63.4	4.7	.3	.2	.1	tr	22.1	2.8	5.2	62.8	4.7	0	.3	.3	.8	48.8	26.6	9.1	8.5	4.7	.6	1.9	0	1840	25.0	77	93	101	19S
19P	13776									0.6																	7	1700	23.0	77	91	101	19P
19Q	13777									.5																	11	1760	23.0	76	96	106	19Q
20S	13778	19.9	3.9	7.5	66.0	1.0	.6	.4	.2	.3	19.9	3.9	7.0	64.7	1.0	0	.5	.2	.8	59.5	12.2	12.0	11.9	1.0	1.3	1.9	2	1700	24.5	83	95	109	20S
20P	13779									1.3																	2	1730	24.5	86	96	109	20P
20Q	13780									1.4																	13	1700	23.0	85	97	115	20Q
21S	13781	20.9	3.0	7.6	66.0	1.3	.3	.4	.2	0.1	20.9	3.0	7.2	65.6	1.3	0	.4	.1	.6	55.6	18.0	14.0	9.1	1.3	0.4	2.5	1	1620	26.5	86	100	108	21S
21P	13782									.4																	5	1720	24.5	89	101	111	21P
21Q	13783									.4																	9	1730	23.5	85	105	112	21Q
22S	13784	21.9	2.6	6.0	63.4	4.4	.2	.2	.2	0	21.9	2.6	5.7	63.1	4.4	0	.3	.5	.9	48.3	26.3	10.7	7.9	4.4	.3	2.3	0	1720	26.5	75	89	95	22S
22P	13785									.3																	3	1740	24.5	81	89	95	22P
22Q	13786									.2																	11	1570	23.5	86	94	100	22Q
23S	13787	19.9	2.5	7.4	65.4	3.1	.4	.3	.2	.9	19.9	2.4	7.0	63.4	3.1	.1	.4	.5	.5	56.3	14.6	14.6	7.3	3.1	2.0	3.0	2	1640	24.5	82	98	105	23S
23P	13788									2.0																	5	1580	23.5	86	97	103	23P
23Q	13789									1.6																	11	1600	23.0	86	104	113	23Q
																											Average of 22 compositions						
S																											0.9	1720	24.3	74.6	86.4	93.9	-------
P																											6.8	1690	23.1	74.7	86.9	95.9	-------
Q																											13.4	1670	22.4	74.7	90.9	101.8	-------

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[1] S, slowly cooled clinker; P, plant clinker; Q, rapidly cooled clinker.
[2] Chemical analyses by C. L. Ford.

When mixing the pastes, it was observed that the cements obtained from the slowly cooled clinker, that is, those of low glass content, generally gave a very stiff paste, and when these pastes were placed in the vials very little or no water came to the surface. With cements of high Al_2O_3/Fe_2O_3 ratio this phenomenon was more pronounced than with cements of low Al_2O_3/Fe_2O_3 ratio. The cements obtained from the rapidly cooled clinker, that is, those of high glass content, always gave a paste which could be poured into vials readily. With these pastes an appreciable quantity of water would come to the surface after standing a few minutes. In the sealed vials this water would be completely reabsorbed by the paste after 24 hours. The cements prepared from the plant clinker gave pastes of intermediate stiffness. These observations are in agreement with the normal consistency data given in table 1. It may be observed that for any given composition the cement prepared from a slowly cooled clinker generally required more water for normal consistency than did the cement prepared from the rapidly cooled clinker, while that from the plant clinker was generally intermediate. It may also be observed from these data that the difference in water required for normal consistency, for the cements of a given composition, was generally greater for compositions of high Al_2O_3/Fe_2O_3 ratio than for compositions of low Al_2O_3/Fe_2O_3 ratio.

III. HEAT OF HYDRATION

The heat of hydration of these cements was determined by the heat-of-solution method using the vacuum-flask calorimeter [5]. Table 1 gives the oxide composition, the calculated compound composition [6, 7] and the approximate glass content of the commercial portland cement clinker compositions from which these cements were prepared. Table 1 also gives the glass content of the same clinker after being subjected to special heat treatments in the laboratory, the specific surface of the cements, the water required for normal consistency, and the heat of hydration at 3, 7, and 28 days.

IV. DISCUSSION

The results obtained from this investigation indicate that the heat evolved up to 28 days during the hydration of portland cements, ground to about the same degree of fineness, is dependent on a number of factors, two of the most important of which are: (1) The composition of the cement, and (2) the glass content of the clinker. The glass content not only influences the heat of hydration directly, but also influences it indirectly, through its effect upon the true compound composition. Changes in the composition of the cement produce greater differences in the heat of hydration than are produced by changes in the glass content.

For the compositions used in this investigation, the heat of hydration at 28 days of the cements prepared from the untreated commercial clinker, ranged from 77 to 111 cal/g, a difference of 34 cal/g. That even larger differences may be obtained by varying the composition of the cement has been indicated by Woods, Steinour, and Starke [8]. From an investigation of laboratory cements of widely different composition, but prepared by uniform burning conditions, they found that the heat of hydration at 28 days ranged from 49.8 to 108.8 cal/g, a maximum difference of 59.0 cal/g.

Considering the change in the heat of hydration due to the presence of glass in the clinker, it was found that although at 3 days, for cements of a given composition but of different glass content, no trend was apparent, at 7 days, with but one exception, the cements of highest glass content had somewhat greater heats of hydration. At 28 days the difference in the heats of hydration (between high and low glass content for any given composition) was even more pronounced than at 7 days, and in every case was greater for the cements of highest glass content. The differences in the 28-day heats of hydration resulting from changes in glass content range from 3 to 16 cal/g with an average of 7.9 cal/g. By comparing the results obtained with different compositions it will be observed that the differences in the heats of hydration are not strictly proportional to the changes in glass content. It seems probable that this may be accounted for from the following considerations: (1) With different clinker compositions the composition of the glass varies; (2) with different clinker compositions a given change of glass content is not always accompanied by identical changes in the compound composition.

Using the factors derived by Woods, Steinour, and Starke [8] for the heat effects due to composition, it is possible to calculate changes in composition which would be equivalent to the effect of the glass content observed in the present investigation. According to these factors the average difference of 7.9 cal/g, between the heat of hydration of the cements having the lowest glass content and those having the highest, could be obtained by the following changes in composition: (1) Maintaining the Al_2O_3 and Fe_2O_3 constant and raising the CaO 0.97 percent and decreasing the SiO_2 0.97 percent, or, expressed in terms of compounds, by increasing the $3CaO.SiO_2$ 11.2 percent and decreasing the $2CaO.SiO_2$ 11.2 percent; (2) by maintaining the CaO and SiO_2 constant and increasing the Al_2O_3 2.6 percent and decreasing the Fe_2O_3 2.6 percent; and (3) by adjusting the oxide composition to maintain the $3CaO.SiO_2$ and $2CaO.SiO_2$ constant and to increase the $3CaO.Al_2O_3$ 5.1 percent and decrease the $4CaO.Al_2O_3.Fe_2O_3$ 5.1 percent. From these calculations it becomes apparent that the differences in the heat of hydration resulting from variations in glass content are equivalent to relatively large changes in composition.

The rate of heat evolution during hydration is also affected by the fineness of the cement. Cement hydrates more rapidly and has a higher heat of hydration at early ages, as its fineness increases. The differences in the fineness of the cements used in this investigation would account for only a very small part of the observed differences in the heats of hydration.

In the absence of complete knowledge of the constitution of portland cement, it is not possible to give a definite explanation for the observed variations in the heats of hydration of cements of different glass content. However, it is possible to point out some factors, each of which may contribute to the observed effects.

1. For the cements used in this investigation an amount of gypsum was added to give a constant content of SO_3 in the cement. It is known that the addition of gypsum affects the hydration processes of portland cement and that this effect is not identical for all cement compositions. It also seems probable that a given quantity of gypsum may not have the same effect for cements of the same composition but of different glass contents. Since the effect of gypsum is most

pronounced at very early ages, this may partly account for the observed phenomenon that at 3 days, and to a lesser degree at 7 days, the heat of hydration did not show a consistent relation to the glass content. At 28 days variations in the heat of hydration, as affected by the gypsum, should be and apparently are less pronounced.

2. Since the glass in portland cement is a metastable phase [9] it should hydrate more rapidly than the corresponding crystalline phases. On this basis the cements of higher glass content would be expected to have higher heats of hydration at early ages; except as influenced by the gypsum and fineness as discussed above.

3. With cements containing glass, the $3CaO.SiO_2$ content generally is different from that of similar cements at crystalline equilibrium. From a study of the quaternary system CaO-Al_2O_3-SiO_2-Fe_2O_3, Lea and Parker [10] found that when the Al_2O_3/Fe_2O_3 ratio is medium or high, cements containing glass will have a higher $3CaO.SiO_2$ content, and a lower $2CaO.SiO_2$ content, than the corresponding cements at crystalline equilibrium. When the Al_2O_3/Fe_2O_3 ratio is low this condition will be reversed. Since $3CaO.SiO_2$ hydrates more rapidly and has a higher heat of hydration than $2CaO.SiO_2$ these changes in the calcium silicate content will have an effect on the heat of hydration at early ages.

4. Cements containing glass have higher heats of solution than do the corresponding cements at crystalline equilibrium. When cements of a given composition, but of varying glass content, are completely hydrated, the total heat of hydration should vary by the same amount as the heat of solution of the original cements, provided the final products of hydration are identical. However, at 28 days the cements are not completely hydrated and it is not definitely known at the present time that cements of a given composition but of different glass contents will hydrate to the same end products.

5. The degree of crystallization of the compounds formed by the alkalies and other minor constituents would also be expected to affect the heats of hydration of the cements. Since the course of crystallization of these minor constituents is not clearly defined at the present time it is not possible to evaluate their effect on the heat of hydration.

V. CONCLUSION

The results of this investigation give further evidence that there are a number of variables which affect the heat of hydration of portland cement. Some of these factors are not fully understood and hence cannot be definitely controlled in present day manufacturing processes. For these reasons it seems desirable that when cement is to meet a specific heat of hydration requirement, dependence should not be placed upon estimates from composition and fineness but the heat of hydration should be actually determined. With the known heat of hydration as a starting point, the manufacturer may make such changes or adjustments of composition and kiln operation as may be necessary to meet the specification requirements.

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