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METHOD FOR APPROXIMATING THE GLASS CONTENT OF PORTLAND CEMENT CLINKER [1]

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ABSTRACT

This report describes a method for approximating the glass content of portland cement clinker. The method involves a determination of the heat of solution of the original clinker and of the same clinker which has subsequently been annealed under conditions designed to produce complete crystallization. The difference between the heat values so obtained is due principally to the latent heat of crystallization of the glass present in the original clinker. The ratio between that value and the latent heat of crystallization of the glass phase represents the glass content of the clinker. A curve is given showing the latent heat of crystallization of all possible glass compositions obtainable from melts at 1,400° C in the system $CaO-Al_2O_3-SiO_2-Fe_2O_3$ between the Al_2O_3/Fe_2O_3 ratios of 0.64 and 3.24.

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I. INTRODUCTION

At the clinkering temperatures attained by present-day methods of portland cement manufacture, a considerable part of the charge is present as a liquid phase, the percentage of liquid produced being dependent on the chemical composition of the charge and on the maximum temperature attained. The disposition of this liquid phase in the clinker is dependent on the subsequent rate of cooling. If the cooling process is sufficiently rapid, a condition may be approached in which the liquid phase will be present as an "undercooled liquid" or glass. But if the cooling process is sufficiently slow to permit a continuous equilibrium, a completely crystalline product may be obtained. Intermediate rates of cooling may produce clinker of some degree of crystallization intermediate between these limits. Furthermore, the relative amounts and nature of the compounds formed on complete crystallization may be somewhat different if the liquid crystallizes independently than if equilibrium with the solid phases is maintained.

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[1] The method should be applied to freshly burned, unhydrated portland cement clinker. It can not be applied to ground cements containing gypsum or to clinker which has been partially hydrated or carbonated.

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The methods of calculation of the compounds in portland cement proposed by Bogue [1] [2] and Dahl [2] are based on the assumption that complete crystalline equilibrium has been attained. A number of reports have been published which indicate that this condition of equilibrium is not consistently attained in the commercial production of portland cement. The work of Rankin and Wright [3] has shown that the gamma form of $2CaO.SiO_2$ is the stable form at ordinary temperatures, whereas in present-day portland cement the $2CaO.SiO_2$ occurs in the beta form. Lea and Parker [4], Forsen [5], Spohn [6], Solacolu [7], and Kuhl [8] have found that the practical limit of lime saturation is lower than the theoretical limit on the basis of complete equilibrium. The presence of glass has also been confirmed by microscopic examination of commercial clinkers. Through microscopic examination by the immersion method and in polished section Insley [9] found certain clinkers to contain several percent of glass and the ratio of $3CaO.SiO_2$ to $2CaO.SiO_2$ in these clinkers to be greater than that obtained by calculation. Miller [10] also has reported the presence of glass in commercial clinker. He found the amount of glass to vary considerably but reported that "there are probably several percent of glass present in even a well-crystallized clinker." From studies of heats of solution of portland cements and portland cement compounds Swenson and Flint [11] found that experimentally obtained heats of solution of the cements are greater than those calculated on the basis of crystalline equilibrium.

Recent investigations reported by Lea and Parker [12, 4] on that portion of the quaternary system $CaO{-}Al_2O_3{-}SiO_2{-}Fe_2O_3$ which covers the region involved in portland cement, provide valuable data for a more complete understanding of the constitution of portland cement. From these data it becomes possible to calculate the quantity and composition of the liquid and crystalline phases which may be present under equilibrium conditions, at any temperature in *this quaternary system* under each of the following three assumptions:

1. That complete crystallization is attained with equilibrium maintained on cooling (calculations according to Bogue and Dahl).
2. That the equilibrium mixture of solid and liquid phases at any specified clinkering temperature is "frozen"; that is, that the liquid is solidified completely as glass.
3. That the crystalline phases at the clinkering temperatures are in equilibrium with their surroundings and remain unchanged while the liquid phase crystallizes independently on cooling.

Calculations based on these three alternatives permit wide variations in the computed constitutions as indicated from the results given in table 1, which is taken from the report of Lea and Parker [4].

It is recognized that the minor constituents of portland cement clinker (MgO) K_2O, Na_2O, MnO, TiO_2 etc.) will influence the equilibrium conditions at clinkering temperatures, and that they will influence the course of crystallization during cooling. The function of these constituents is not yet known and hence can not be definitely evaluated at the present time.

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[2] Numbers in brackets refer to references at the end of this paper.

TABLE 1.—*Comparison of computed clinker compositions under different conditions of solidification*

(From Lea and Parker [4])

$C_3S=3CaO.SiO_2$.
$C_2S=2CaO.SiO_2$.
$C_3A=3CaO.Al_2O_3$.
$C_4AF=4CaO.Al_2O_3.Fe_2O_3$.
$C_5A_3=5CaO.3Al_2O_3$.

Constituents	Complete equilibrium crystallization	Crystallization at 1,400° C. Liquid gives glass	Crystallization at 1,400° C. Liquid crystallizes independently	Crystallization at 1,450° C. Liquid gives glass	Crystallization at 1,450° C. Liquid crystallizes independently
I. $CaO=68.0\%$, $SiO_2=23.0\%$, $Al_2O_3=6.0\%$, $Fe_2O_3=3.0\%$. $Al_2O_3/Fe_2O_3=2.0$					
	%	%	%	%	%
C_3S	57.5	59.6	59.6	59.6	59.6
C_2S	22.5	16.2	21.2	15.6	21.0
C_3A	10.8	0	8.9	0	9.8
C_4AF	9.1	0	9.1	0	9.1
C_5A_3	0	0	1.0	0	0.5
Glass	0	24.3	0	24.8	0
II. $CaO=68.0\%$, $SiO_2=23.0\%$, $Al_2O_3=7.0\%$, $Fe_2O_3=2.0\%$. $Al_2O_3/Fe_2O_3=3.5$					
C_3S	52.2	60.6	60.6	59.4	59.4
C_2S	26.5	15.4	20.9	15.3	21.4
C_3A	15.2	0	9.4	0	9.7
C_4AF	6.1	0	6.1	0	5.9
C_5A_3	0	0	3.8	0	3.8
Glass	0	25.1	0	25.5	0
III. $CaO=66.0\%$, $SiO_2=24.0\%$, $Al_2O_3=7.5\%$, $Fe_2O_3=2.5\%$. $Al_2O_3/Fe_2O_3=3.0$					
C_3S	32.4	38.2	38.2	38.5	38.5
C_2S	44.5	34.3	40.2	33.3	39.9
C_3A	15.7	0	10.5	0	10.6
C_4AF	7.6	0	7.6	0	7.6
C_5A_3	0	0	3.6	0	3.5
Glass	0	27.6	0	28.1	0
IV. $CaO=67.0\%$, $SiO_2=23.0\%$, $Al_2O_3=4.0\%$, $Fe_2O_3=6.0\%$. $Al_2O_3/Fe_2O_3=.67$					
C_3S	62.7	54.6	60.9	55.1	61.5
C_2S	18.6	20.2	20.2	19.4	19.4
C_3A	0.5	0	0.4	0	0.5
C_4AF	18.2	0	18.2	0	18.2
CaO	0	0	0.3	0	0.7
C_5A_3	0	0	0	0	0
Glass	0	25.0	0	25.5	0

Under present commercial conditions of cement manufacture it seems improbable that the cooling conditions would be sufficiently rapid to completely "freeze" the liquid into glass, and it seems unlikely that the cooling conditions would be sufficiently slow to attain complete crystalline equilibrium. Thus it seems probable that most portland cement clinker would be in some intermediate state. The most rapidly cooled clinker may approach the composition computed on the assumption that the liquid freezes to glass; and the most slowly cooled clinker may approach the composition computed on the assumption of complete crystalline equilibrium.

Numerous attempts to correlate the properties of commercial portland cements with their oxide composition, or computed compound composition, have met with only partial success. The discrepancies suggest that the glass content of the clinker may have an important effect on some of the properties of the cement. A primary requirement for any investigation of the effect of the glass is the availability of a method of estimating the glass content of the clinker. The present report describes a heat of solution method for approximating the glass content of portland cement clinker.

II. EXPERIMENTAL PROCEDURE

1. PREPARATION OF COMPOSITIONS CORRESPONDING TO THE LIQUID PHASE AT 1,400° C

The method employed for the approximation of glass content of portland cement clinker is dependent on the latent heat of crystallization[3] of the liquid present at the clinkering temperature. From the work of Lea and Parker [4] it is possible to calculate the quantity of liquid and the composition of the liquid phase of any portland cement mixture in the system $CaO-Al_2O_3-SiO_2-Fe_2O_3$ when in equilibrium at any clinkering temperature. For most cements, the liquid composition at 1,400° or 1,450° C lies within the $3CaO.SiO_2$ primary phase volume, or on its boundary surfaces with $2CaO.SiO_2$ or CaO. At these temperatures the composition of the liquid phase of these cements will be largely dependent on the Al_2O_3/Fe_2O_3 ratio, and the

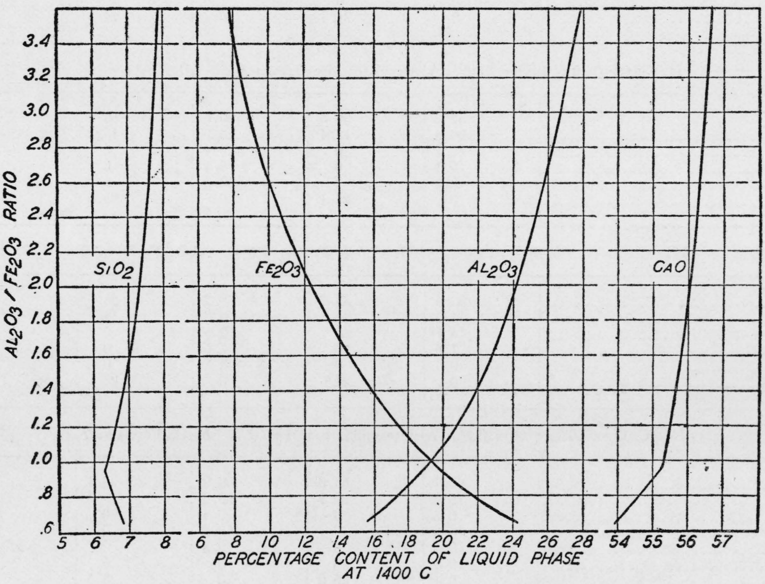

FIG. 1.—*Oxide composition of liquid at 1,400° C.*

(Lea and Parker).

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[3] The latent heat of crystallization is the difference in heat content between the crystalline and noncrystalline state of a system at the temperature at which crystallization occurs. In the method described this difference in heat content is determined by the heat of solution method at a temperature below that at which crystallization occurs. For convenience this difference is referred to as latent heat of crystallization.

quantity of liquid will be dependent on the quantities of Al_2O_3 and Fe_2O_3. The composition of the liquid at 1,400° C in the quaternary system CaO–Al_2O_3–SiO_2–Fe_2O_3, for any given Al_2O_3/Fe_2O_3 ratio between 0.64 and 3.6 may be obtained from figure 1.[4]

The clinkering temperature of most portland cements is probably between 1,400° and 1,450° C. Between these temperatures there are only slight changes in the composition of the liquid or in the quantity of liquid for any given cement composition. (See table 1.) Accordingly, a number of mixtures were prepared which were representative of the composition of the liquid phase at 1,400° C for various Al_2O_3/Fe_2O_3 ratios in the system CaO–$2CaO.SiO_2$–$5CaO.3Al_2O_3$–$4CaO.Al_2O_3.Fe_2O_3$. In some instances similar compositions were prepared with the addition of 8.0 percent of MgO. These compositions, listed in table 2, were used for the determination of the latent heat of crystallization.

TABLE 2.—*Latent heat of crystallization of liquid compositions of varying* Al_2O_3/Fe_2O_3 *ratio on the* C^3S-C^2S *surface at 1400°C.*

No.	Oxide composition						Potential compound composition at crystalline equilibrium							Calculated heat of solution of pure compounds	Crystalline material	Quenched compositions	Differences in obtained values	Correction for inversion of C_2S	Latent heat of crystallization
	CaO	MgO	Al_2O_3	Fe_2O_3	SiO_2	Al_2O_3/Fe_2O_3	C_3A	C_5A_3	C_4AF	C_3S	λC_2S	CaO	MgO						
	%	%	%	%	%	%	%	%	%	%	%	%	%	cal/g	cal/g	cal/g	cal/g	cal/g	cal/g
1R	53.9	----	15.3	24.0	6.8	0.64	----	----	73.0	25.8	----	1.3	----	602.1	601.0	637.0	36.0	0	36.0
2	55.2	----	18.7	19.9	6.3	0.94	15.8	----	60.5	23.8	----	----	----	629.2	629.0	672.0	43.0	0	43.0
3	55.7	----	23.5	13.9	6.9	1.7	35.8	2.1	42.3	----	19.8	----	----	654.4	653.5	702.0	48.5	1.2	47.3
4	56.2	----	24.6	12.3	7.0	2.0	38.0	4.5	37.4	----	20.1	----	----	662.0	663.7	714.7	51.0	1.2	49.8
5	56.3	----	26.2	10.0	7.6	2.62	35.6	12.2	30.4	----	21.8	----	----	667.2	672.5	720.3	47.8	1.3	46.5
11	56.5	----	27.2	8.4	7.7	3.24	37.1	15.0	25.5	----	22.2	----	----	673.1	673.5	725.1	51.6	1.3	50.3
6R	49.6	8.0	14.1	22.1	6.3	0.64	----	----	67.2	23.7	----	1.2	8.0	623.9	625.6	660.3	34.7	0	34.7
8	51.2	8.0	21.6	12.8	6.3	1.7	32.9	1.9	38.9	----	18.2	----	8.0	671.3	672.1	719.7	47.6	1.1	46.5
10	51.8	8.0	24.1	9.2	7.0	2.62	32.7	11.2	28.0	----	20.1	----	8.0	683.7	684.9	736.0	51.1	1.2	49.9

The compositions, prepared from intimate mixtures of chemically pure calcium carbonate, alumina, silica, ferric oxide, and magnesia, were heated in an electric furnace at 1,250° C for 1 hour and reground as a further precaution to obtain uniformity. Quenched and crystalline preparations were then made by the special heat treatments described below.

The quenched samples were prepared by quenching the liquid in mercury. A few grams of a given composition were wrapped in platinum foil and suspended in an electrically heated quenching furnace. The furnace was then heated to 1,450±10° C and held at that temperature for 15 minutes to permit complete melting of the charge. The charge was then dropped from the furnace and immersed in mercury to obtain rapid cooling. The preparations were considered to be a satisfactory glass when they were found by microscopic examination to be vitreous, nearly or quite homogeneous, and to contain very little or no birefracting material.

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[4] The composition for the Al_2O_3/Fe_2O_3 ratio 0.64 as given in the text of the report by Lea and Parker is incorrect. The composition as used in figure 1 has been confirmed by personal correspondence with Lea.

The crystallized materials were prepared by carefully "annealing" [5] the charge in an electric furnace. The compositions were placed in the furnace and heated to 1,400° C. The temperature of the furnace was then caused to drop slowly over a period of 2 hours to 1,250° C, which is below the temperature of formation of liquid, and the charge was held at that temperature ±10° C for 15 hours.

The compositions which were computed to contain $2CaO.SiO_2$ at crystalline equilibrium all "dusted" after annealing because of the inversion of the beta $2CaO.SiO_2$ to the gamma form. The compositions which were computed not to contain $2CaO.SiO_2$ at crystalline equilibrium did not "dust."

Examinations for free lime were made on each of the quenched and crystallized compositions by White's [13] method and by the ammonium acetate method [14]. All quenched compositions gave negative results by both methods, which indicated the absence of free lime. The crystalline compositions no. 1R and no. 6R (table 2) contained 1.5 and 1.0 percent of free lime, respectively. The other crystalline compositions contained no free lime.

2. MICROSCOPIC AND X-RAY EXAMINATION OF THE GLASS

The quenched preparations were examined microscopically. They appeared vitreous with small amounts of birefracting material, particularly in the samples with low Al_2O_3/Fe_2O_3 ratios, which contained some glassy material showing evidences of strain. The index of refraction of all of the material in any one sample was not uniform but varied through the sample. Regrinding and requenching of the samples did not eliminate this variation of index of refraction. The extent of variation was dependent on the rate of cooling and on the composition. Compositions with high Al_2O_3/Fe_2O_3 ratios showed less variation than those with low Al_2O_3/Fe_2O_3 ratios. And those quenches which were immersed in mercury entirely on falling from the furnace showed less variation than those which floated on the surface of the mercury for a fraction of a second before submersion by pushing them into it by hand. Much smaller charges (0.1 g or less) were then quenched but in no case was it possible to eliminate the variation in index of refraction entirely, even under conditions of most rapid cooling of very small samples, although under these conditions the variation was at a minimum.

The following values were obtained for the index of refraction of a small quenched charge of composition 11 (table 2) with Al_2O_3/Fe_2O_3 ratio=3.24. Some of the material had an index of refraction as low as 1.724 ± 0.003 (red light). But the index of the greater portion of the sample was slightly higher, between 1.724 and 1.734. There was present also some material with an index which was as high as 1.755 ± 0.005. A quenched charge of composition 1R with Al_2O_3/Fe_2O_3 ratio=0.64 contained material with an index of 1.83 ± 0.01, and some material with an index as high as 1.92 ± 0.01.

Powder X-ray diffraction patterns were made of the quenched preparations used for the determination of the heat of solution. Diffraction lines were obtained from all preparations, which in general corresponded almost exactly with the cubic lines of crystalline $3CaO.Al_2O_3$. The strongest diffraction patterns were obtained from

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[5] The term "annealing", as used in this report, involves a slow cooling process which might be expected to produce a maximum degree of crystallization.

the samples with the lower Al_2O_3/Fe_2O_3 ratios; samples 1R and 6R had the most intense patterns of the entire series of compositions given in table 2.

Figure 2 (A) is a reproduction of the X-ray pattern of composition 1R compared with that of $3CaO.Al_2O_3$. The lines of the two patterns are almost identical in position and relative intensity. This might be taken as evidence that $3CaO.Al_2O_3$ is present in composition 1R. However, the following facts are not in entire agreement with such an interpretation:

1. Sample 1R represents a composition in the ternary system CaO-$2CaO.SiO_2$-$4CaO.Al_2O_3.Fe_2O_3$. According to all experimental data published to date, $3CaO.Al_2O_3$ does not exist at equilibrium in any portion of that system.
2. The compounds of CaO and Fe_2O_3 usually crystallize much more rapidly than the compounds of CaO and Al_2O_3. Accordingly, the tendency would be for the crystallization of some compound of ferric oxide first of all under the cooling conditions outlined and not for the crystallization of $3CaO.Al_2O_3$.
3. The quenched compositions low in Al_2O_3 show very strong X-ray diffraction patterns, while those high in Al_2O_3, and consequently high in calculated $3CaO.Al_2O_3$, show much weaker patterns. If the diffraction lines were caused by $3CaO.Al_2O_3$, we should expect the compositions high in calculated $3CaO.Al_2O_3$ to show the more intense patterns.
4. The X-ray diffraction pattern of a mixture of $2CaO.SiO_2$ and $2CaO.Fe_2O_3$, when quenched from temperatures at which the mixture is liquid, is that of a cubic crystal with lines practically identical in position with the lines of composition 1*R* (fig. 2 (*B*)).[6] Accordingly, mixtures of CaO, SiO_2, and Fe_2O_3 also show a crystalline structure similar to that of $3CaO.Al_2O_3$, so that apparently we cannot rely on the X-ray alone for identification of that compound.

Considering these facts there is some doubt as to the existence of $3CaO.Al_2O_3$ in the quenched liquids. Further work is in progress to identify the phase in the quenched charges corresponding to the liquid phase of cement clinker, which shows the cubic structure. This material has been commonly called "glass" in the past, and the use of that term is continued here.

In rapidly cooled clinker the glass phase may be in a state comparable with that of the glasses quenched for these determinations of heat of solution and therefore cause diffraction lines in the X-ray pattern in positions corresponding to those of $3CaO.Al_2O_3$. If the lines obtained from the glasses are not due to the presence of $3CaO.Al_2O_3$, as now seems probable but with confirmation still missing, then $3CaO.Al_2O_3$ may have been erroneously identified in some of the cement clinker, as reported in a paper by Brownmiller and Bogue [15].

3. LATENT HEAT OF CRYSTALLIZATION OF THE LIQUID PHASE

The heats of solution of the quenched and crystalline materials were determined by the use of a vacuum-flask calorimeter [16]. The heats of solution were determined at room temperature, 23±3° C. The difference between the heat of solution of the quenched materials and the crystalline materials corrected for the heat evolved by the beta to gamma inversion of dicalcium silicate is recorded as the latent

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[6] Diffraction lines of platinum are present in the pattern of the $2CaO.SiO_2$-$2CaO.Fe_2O_3$ mixture because of contamination by the platinum foil in which the charge was enclosed.

heat of crystallization. The results of the determinations of the heats of solution and the latent heats of crystallization are given in table 2. Each value for heat of solution is the mean of duplicate determinations, which agreed to within 3.0 cal/g in every case. With the quenched compositions the duplicate determinations of heat of solution were made on separate quenches of the same composition.

The heat of solution was also determined of the compounds which would be present at crystalline equilibrium for the compositions given in table 2. These compounds were prepared by heating the appropriate mixtures below the temperature of formation of liquid for sufficient time to attain complete combination. By this process the compounds were assumed to have been obtained in a completely crystalline condition. The solvent used for the heat of solution determinations was 420 g of 2 *N* HNO_3 containing 5 ml of 48-percent HF, which was found to be satisfactory for attaining complete solution of 3-g samples of all of the compounds used in this investigation. The same solvent was used for determining the heats of solution of the various compositions given in table 2. The heats of solution of the several compounds are given in table 3. The heats of solution, obtained in this manner, of some of these compounds are different from values given in a previous report [17], which is due to the use of different solvents.

TABLE 3.—*Heat of solution of cement compounds* [1]

Cement compounds	Heat of solution [2]
	cal/g
C_3A	783.3
C_5A_3	726.2
C_4AF	586.8
C_3S	632.0
γC_2S	556.8
βC_2S (with 0.4% of B_2O_3)	563.0
CaO	835.0
MgO	875.4

[1] 3 g dissolved in 420 g of 2 *N* HNO_3 containing 5 ml of 48-percent HF.

[2] The heats of solution were at room temperature, 23 ±3° C. The estimated uncertainty of these values was ±2.0 cal/g.

From the heats of solution of the several compounds it should be possible to calculate the heats of solution of the crystallized compositions listed in table 2. These values have been calculated and are given in the table. The close agreement between the calculated values and the determined values for the heats of solution of these crystalline compositions gives supporting evidence to indicate that nearly complete crystallization has been attained.

The latent heats of crystallization of the compositions containing 8.0 percent of MgO were found to be nearly the same as those of the corresponding compositions containing no MgO, (compare 1R and 6R, 3 and 8, 5 and 10). This indicates that the presence of MgO up to 8.0 percent does not materially change the latent heat of crystallization of these compositions. The 8.0 percent of MgO used in these compositions would correspond to 2.0 percent of MgO in a cement composition containing 25 percent of liquid at the clinkering temperature. By microscopic examination of the quenched samples prepared from the compositions containing 8.0 percent of MgO, it was found in each composition that some MgO was present as periclase. This

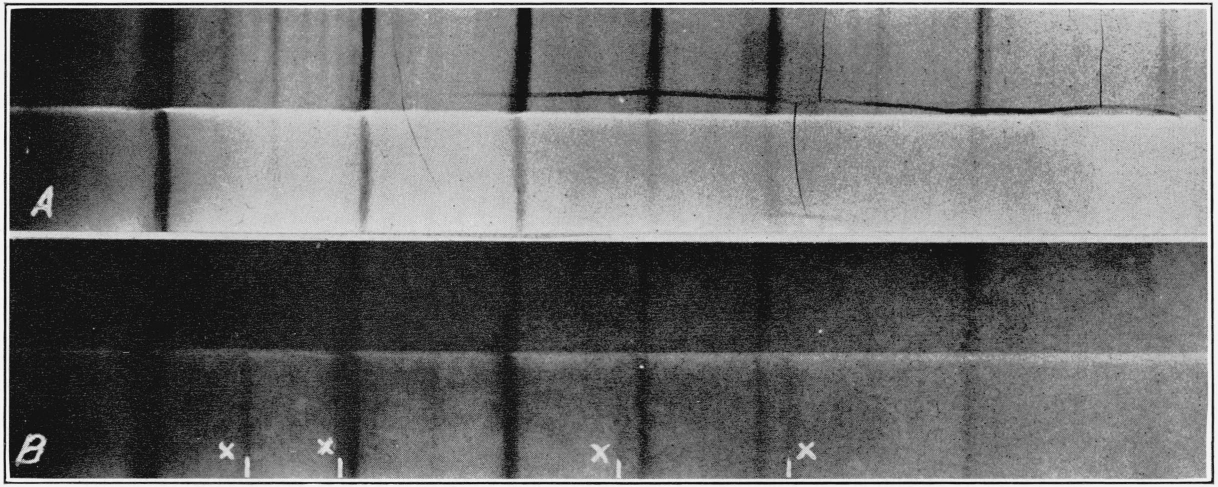

FIGURE 2.—*X-ray pattern of crystalline* $3CaO.Al_2O_3$ *and quenched-liquid compositions.*

(*A*). Upper—Pattern of crystalline $3CaO.Al_2O_3$. Lower—Pattern of composition *1R* (table 2) consisting of 53.9% of CaO, 15.3% of Al_2O_3, 6.8% of SiO_2, 24.0% of Fe_2O_3 quenched from 1,450° C.

(*B*). Upper—Pattern of composition *1R* (table 2) consisting of 53.9% of CaO, 15.3% of Al_2O_3, 6.8% of SiO_2, 24.0% of Fe_2O_3 quenched from 1,450° C. Lower—Pattern of composition consisting of 45.9% of CaO, 7.0% of SiO_2, 47.1% of Fe_2O_3 quenched from 1,540° C.

x—Indicate platinum lines.

seems to indicate that liquids of these compositions do not dissolve as much as 8.0 percent of MgO at 1,450° C.

In the study of the system $2CaO.SiO_2$–MgO–$5CaO.3Al_2O_3$ Hansen [18] found that melting occurs at 1,315° C, and that MgO dissolves readily and extensively, up to 7.0 percent, in the liquid formed at 1,315° C or at higher temperatures. When the charges were cooled rapidly the liquid was converted to a glass and the MgO remained in solution in this glass. The solubility of the MgO in the liquid of the system CaO–MgO–$2CaO.SiO_2$–$5CaO.Al_2O_3$ was found by McMurdie and Insley [19] to vary from 5 to 33 percent but, in the region of portland cement to fall between 6 and 18 percent. Brownmiller [20] has found that at 1,400° to 1,450° C about 4 to 6 percent of MgO dissolves in the liquid of the CaO–Al_2O_3–SiO_2–Fe_2O_3 system having Al_2O_3/Fe_2O_3 ratios between 0.68 and 3.0. The solution of MgO in the liquid phase of portland cement clinkers is also indicated by Lea and Parker [4].

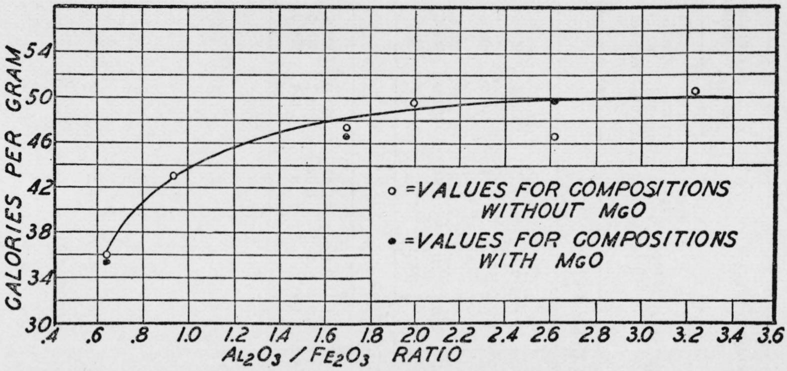

FIGURE 3.—*Latent heat of crystallization of liquid compositions of varying alumina: ferric oxide ratios on the tricalcium silicate-dicalcium silicate surface at 1,400° C.*

The latent heats of crystallization of the compositions given in table 2 are shown in figure 3 plotted against the Al_2O_3/Fe_2O_3 ratios. The latent heats of crystallization of compositions of other Al_2O_3/Fe_2O_3 ratios not given in table 2 may be obtained from figure 3.

4. APPROXIMATION OF THE GLASS CONTENT OF PORTLAND CEMENT CLINKER

Having determined the latent heat of crystallization of the liquid compositions of varying Al_2O_3/Fe_2O_3 ratio, it remained to apply these data in the development of a method for approximating the glass content of portland cement clinker. A group of laboratory compositions of various Al_2O_3/Fe_2O_3 ratios was selected for study. The clinker of these compositions was prepared from commercial raw materials and burned in an experimental rotary kiln. The clinker obtained from this kiln is usually small, about ¼ to ½ inch in diameter, and, in the usual process of operation, is cooled from the clinkering temperature to about 1,000° C in 2 or 3 minutes. These clinkers are referred to in table 4 as "rapidly cooled." In some cases clinkers of corresponding compositions were heated in an auxiliary furnace at 1,100° C for 3 to 4 hours. These clinkers are referred to as "specially treated."

TABLE 4.—*Approximate glass content of laboratory clinkers of varying* Al_2O_3/Fe_2O_3 *ratio*

No.	Method of cooling	Partial oxide composition					Potential crystalline compound composition						Al_2O_3/Fe_2O_3 ratio	Calculated heat of solution at crystalline equilibrium	Obtained heat of solution		Difference		Approximate glass content	Quaternary liquid content at 1,400° C
		CaO	MgO	Al_2O_3	Fe_2O_3	SiO_2	C_3A	C_4AF	C_3S	γC_2S	MgO	Free CaO			Original clinker	Annealed clinker	Obtained	Correction for inversion of C_2S		
		K3 CLINKERS																		
		%	%	%	%	%	%	%	%	%	%	%		*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	%	%
5F	Rapid	64.7	3.7	7.0	2.0	22.1	15.1	6.1	45.5	29.0	3.7	0.0	3.5	635.5	644.6	632.8	11.8	10.1	20	25.0
5E	Specially treated [1]	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	647.7	637.8	9.9	8.2	16	25.0
8F	Rapid	66.6	3.0	6.8	2.0	21.0	14.7	6.1	61.0	14.3	3.0	.5	3.4	646.6	659.8	650.3	9.5	8.6	17	24.4
8E	Specially treated	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	656.0	650.3	5.7	4.8	10	24.4
25F	Rapid	63.3	5.0	5.9	3.2	22.2	10.3	9.7	45.0	30.0	5.0	.0	1.84	632.9	644.0	631.9	12.1	10.3	21	24.4
25E	Specially treated	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	641.8	631.3	10.5	8.7	18	24.4
		K2 CLINKERS																		
233	Rapid	62.6	3.1	7.4	5.1	21.2	11.0	15.5	36.7	33.0	3.1	0.0	1.45	620.0	626.8	614.0	12.8	10.8	23	33.0
10a	do	65.0	3.0	4.6	4.5	22.6	4.6	13.6	53.5	24.5	3.0	.5	1.02	620.7	631.5	621.1	10.4	8.9	20	23.5
225	do	61.1	3.1	7.4	8.4	19.3	5.4	25.6	40.4	24.8	3.1	.5	.88	613.4	624.6	611.3	13.3	11.8	28	40.2

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[1] Specially treated clinker was heated at 1,100° C for 3 to 4 hours.

The heats of solution were determined of samples of clinker as prepared by these two methods. A quantity of the clinker prepared by each method was annealed in an electric furnace by heating to 1,400° C and allowing the temperature to decrease slowly over a 2-hour period to 1,250° C, which is below the temperature of formation of liquid. The charge was then held at 1,250° ±10° C for 15 hours, following which the heats of solution were determined. The results are given in table 4, together with the partial oxide composition and the potential compound composition at crystalline equilibrium. Each value for the heat of solution is the mean of duplicate determinations which agreed to within 3.0 cal/g in every case.

The original clinker as prepared in the rotary kiln had not dusted and in this clinker the $2CaO.SiO_2$ was in the beta form. When the clinker was annealed in the electric furance dusting occurred on cooling and by microscopic examination the $2CaO.SiO_2$ was found to be mostly or entirely in the gamma form. Johannson and Thorvaldson [21] have reported that the heat evolved in the transition of $2CaO.SiO_2$ from the beta to gamma modification is 6.0 cal/g at 20° C. This value is in approximate agreement with the difference between the heats of solution of the beta and gamma $2CaO.SiO_2$ reported in table 3. However, the beta $2CaO.SiO_2$ referred to in that table contained a small amount of boric oxide (added to prevent inversion) so that the difference between these values may not indicate precisely the heat evolved on inversion of the beta to the gamma form. Obviously this inversion will bring about a decrease in the heat of solution of the annealed (dusted) samples below that of the original clinkers by 0.06 cal/g per percent of $2CaO.SiO_2$ present.

Table 4 gives the observed heats of solution of the original clinker and of the annealed clinker, the differences between these heats of solution, and these differences corrected for the heat evolved on the inversion of the $2CaO.SiO_2$. This corrected value for the difference between the heat of solution of the original clinker and the annealed clinker is assumed to represent the latent heat of crystallization of the glass present in the original clinker. The approximate glass content of the original clinker was then obtained by dividing this corrected difference in the heats of solution, by the latent heat of crystallization of a liquid composition of the Al_2O_3/Fe_2O_3 ratio of that clinker as obtained from figure 3. For conversion to percentage glass content this quotient was multiplied by 100. Table 4 also contains the quaternary liquid content at 1,400° C, for these clinkers, as calculated from Lea and Parker [4].

It is recognized that certain errors are involved in this method of approximating the glass content of portland cement clinker. The more important sources of error involved in the method are due to: (1) The thermal changes involved in the secondary reactions which occur during the process of crystallization; and (2) the variation in the latent heat of crystallization of an intermediate glass due to the change which may occur in the Al_2O_3/Fe_2O_3 ratio if the several constituents do not crystallize at a uniform rate. The relative magnitudes of these errors may be estimated, but they can not be determined precisely because of lack of definite information as to the extent to which these reactions occur.

The latent heats of crystallization of liquid compositions as given in table 2, and figure 3 represent the thermal changes involved when these compositions crystallize independently. But with cements having Al_2O_3/Fe_2O_3 ratios above 1.6, the liquid may interact with the solid phases, provided the cooling is sufficiently slow, to produce different percentages of some compounds. The order of difference may be noted by comparing the data in columns 1 and 3 in table 1. When the liquid crystallizes independently (column 3 of table 1) $5CaO.3Al_2O_3$ is formed, but in crystallization to complete equilibrium (column 1 of table 1) the alumina has combined with lime derived from the $3CaO.SiO_2$ to form $3CaO.Al_2O_3$; consequently the $3CaO.Al_2O_3$ content of the product is increased, the $3CaO.SiO_2$ decreased, and the $2CaO.SiO_2$ increased. These secondary reactions involve thermal changes the order of which may be approximated from a consideration of the heat effects of the principal changes involved.

By use of the heats of solution given in table 3, it is possible to calculate the heat of formation of $3CaO.Al_2O_3$ from $5CaO.3Al_2O_3$ and CaO. This reaction involves the absorption of 27.0 cal/g of $3CaO.Al_2O_3$ formed. Johannson and Thorvaldson [21] have reported that the formation of $3CaO.SiO_2$ from beta $2CaO.SiO_2$ and CaO involves an absorption of 2.06 cal/g of $3CaO.SiO_2$ formed. It requires 0.277 g of CaO to combine with $5CaO.3Al_2O_3$ to form 1 g of $3CaO.Al_2O_3$; and it requires 1.13 g of $3CaO.SiO_2$, dissociating to $2CaO.SiO_2$ and CaO to supply 0.277 g of CaO. Hence the dissociation of the $3CaO.SiO_2$ involved in the formation of 1 g of $3CaO.Al_2O_3$ results in the liberation of $2.06 \times 1.13 = 2.3$ cal. The net thermal change caused by the formation of $3CaO.Al_2O_3$ is an absorption of $27.0 - 2.3 = 24.7$ cal/g of $3CaO.Al_2O_3$, or 0.247 cal/g of clinker for each percent of $3CaO.Al_2O_3$ produced from the $5CaO.3Al_2O_3$. Since these reactions involve an absorption of heat and the independent crystallization of the liquid phase involves an evolution of heat, the applications of corrections for these secondary reactions would give values somewhat lower than the uncorrected figures.

The liquid phase at clinkering temperatures forms several crystalline compounds when slowly cooled, but except at the eutectic composition these compounds do not crystallize at a uniform proportionate rate. Thus when partial crystallization occurs the remaining liquid may not retain the composition or Al_2O_3/Fe_2O_3 ratio of the original liquid. Since the latent heat of crystallization varies with the Al_2O_3/Fe_2O_3 ratio, and the former is used (fig. 3) in approximating the glass content, it follows that the approximate glass content may be in error in proportion to the change in the Al_2O_3/Fe_2O_3 ratio of the liquid brought about by the partial crystallization.

Lea and Parker [4] have found that when the Al_2O_3/Fe_2O_3 ratio is above 1.38, $3CaO.Al_2O_3$ crystallizes on cooling, until the Al_2O_3/Fe_2O_3 ratio of the remaining liquid is 1.38, at which point $3CaO.Al_2O_3$ and $4CaO.Al_2O_3.Fe_2O_3$ crystallize together. If the ratio is below 1.38, the $4CaO.Al_2O_3.Fe_2O_3$ crystallizes until the ratio of 1.38 is reached. Thus, the liquid of clinker at 1,400° C, having an Al_2O_3/Fe_2O_3 ratio of 2.6, has (by fig. 3) a latent heat of crystallization of 50.0 cal/g. If partial crystallization of the liquid occurs so that the ratio in the remaining liquid is reduced to 1.5, the latent heat of crystallization of the liquid is reduced to 47.0 cal/g. If the observed difference in heats of solution of the original and annealed clinker is 5.2 cal/g, the approximate glass content would be $(5.2 \times 100)/50.0 = 10.4$ percent, whereas the correct glass content should be (5.2×100)/47.0=11.0 percent.

Experimental errors which may occur include those which would result from incomplete inversion of the $2CaO.SiO_2$ to the gamma modification during annealing, and errors in the determination of the heats of solution. These errors can be reduced to low magnitude by careful experimental manipulations. Other sources of error may occur from: absence of information on the exact amount of beta $2CaO.SiO_2$ which may be in the original clinker; failure to attain complete equilibrium at clinkering temperatures in the kiln; thermal changes resulting from the formation of solid solutions; and thermal changes resulting from alkalies, titania, manganese, and other minor constituents of commercial clinker.

Consideration has been given to the possibility of approximating the glass content of a portland cement clinker from the difference between the calculated heat of solution at crystalline equilibrium (calculated from the additive values of the heats of solution of the several crystalline compounds), and the obtained heat of solution of the clinker. Thus, the necessity of the annealing process and the subsequent determination of the heat of solution of the annealed sample would be eliminated. The calculated heats of solution at crystalline equilibrium are given in table 4, for the clinkers used in this investigation. In some instances these calculated values are in good agreement with the obtained heats of solution of the corresponding annealed samples, but in some instances there are rather large discrepancies. There are several factors involved which may account for these discrepancies among which may be mentioned: (1) Portland cement clinker contains varying quantities of minor constituents, alkalies, manganese, titania, etc., which can not, at present, be accounted for in these calculations of the heats of solution at crystalline equilibrium; (2) small errors in chemical analysis result in relatively large variations in calculated compounds; and (3) lack of homogeneity of the clinker. From these considerations it seems probable that more accurate results will follow the use of the value of the heat of solution obtained on the annealed clinker than from the use of the calculated value.

III. SUMMARY AND CONCLUSIONS

This report describes a heat of solution method for approximating the glass content of portland cement clinker. The method involves a determination of the heat of solution of the original clinker and of the same clinker which has subsequently been annealed under conditions designed to produce complete crystallization. The difference between these heats of solution is dependent upon the latent heat of crystallization of the liquid phase which would be present at clinkering temperatures. The latent heat of crystallization has been determined for several liquid phase compositions of varying Al_2O_3/Fe_2O_3 ratios, and from a curve drawn through these points (fig. 3) the latent heat of crystallization of liquid phase compositions of other Al_2O_3/Fe_2O_3 ratios may be obtained.

The method should be applied to freshly burned, unhydrated portland cement clinker. It cannot be applied to ground cements containing gypsum or to clinker which has been partially hydrated or carbonated.

The method involves certain errors for which exact correction factors cannot at present be applied. From a consideration of the nature and magnitude of these errors it seems probable that for the compositions studied the approximate glass contents, as obtained by this method, were correct to within ±5 percent of the total sample.

The results obtained by this method, when applied to a number of laboratory clinkers prepared in an experimental rotary kiln from commercial raw materials, indicate that rapidly cooled portland cement clinker may contain a considerable quantity of glass.

From a comparison of the glass content of the rapidly cooled clinker and of the corresponding specially treated clinker (heated 3 to 4 hours at 1,100° C) it was observed that the glass content of the specially treated clinker was only slightly lower than that of the rapidly cooled clinker. This seems to indicate that heating for 3 to 4 hours at temperatures appreciably below the temperature of formation of liquid does not promote rapid crystallization.

The quenched liquid compositions, which are referred to as glass, were examined microscopically and by X-rays. Under practical cooling conditions it was impossible to solidify the liquids so that they showed no X-ray diffraction pattern. The diffraction pattern obtained was similar to the pattern obtained from $3CaO.Al_2O_3$. A similar pattern has also been obtained from quenched compositions of CaO-Fe_2O_3-SiO_2 which contained no Al_2O_3. The exact nature of the structure which gives this pattern is still in doubt.

The data contained in this report were obtained with experimental clinker and it was not determined how representative they are with respect to commercial clinker.

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