

would not survive this type of drying, and would be altered to C_4AH_{13} . Dry organic liquids such as ethyl alcohol, acetone, etc., when used repeatedly in washing a given sample may dehydrate some of the hydrates. For this reason only one washing with acetone was used. This procedure may not be the best, but so far as results of preliminary tests described above show, the samples did not appear either to be underdried or overdried.

A second problem is that of carbonation. Facilities with CO_2 -free air were not available. The extent of carbonation was minimized by the rapid handling of large samples (about 100g) during exposure to air. DTA results on the pastes, compared to DTA results on blends of known amounts of a CO_2 -free cement paste and calcite, indicated that two of the thirty samples contained 0.4-0.5 percent CO_2 , three contained 0.2 percent or slightly less, and the remainder 0.1 percent or less. About half of the samples showed no calcite endotherm when tested at 100-percent sensitivity; the threshold content for detection was 0.05 percent CO_2 as calcite at this sensitivity.

The samples in polyethylene vials were stored in a desiccator over ascarite. Samples in polyethylene vials deliberately exposed to air for 1 year were found carbonated to the extent of 0.2 to 1.0 percent CO_2 .

THE QUANTITATIVE DETERMINATION OF ALITE AND BELITE RESIDUES IN PARTLY HYDRATED CEMENT PASTES

David L. Kantro, Portland Cement Association

The work to be described in this report is a part of the cooperative program on Evaluation of Methods of Identifying Phases of Cement Pastes, sponsored by the Transportation Research Board Committee A2E06. Although the present results pertain to a method of analysis, rather than identification, the data were obtained by an X-ray method, and consequently lie within the scope of the program.

The method used has been reported previously (1) and has been applied to partly-hydrated pastes by Copeland (2).

The present results include alite and belite contents as functions of age for pastes of three different cements used in the A2E06 program. The study was limited to these two major contributors to cementitious properties.

Experimental

The three cements used in this investigation, and their oxide compositions, were provided by G. L. Kalousek. The oxide compositions of these cements are given in Table 1. One of the three is a normal cement, one is a white cement, and one is a nominal zero-percent- C_3A cement. The first two were of the same brands, but not from the same lots, as the samples used by other investigators on the program. The oxide compositions in these two cases differed slightly, but not significantly, from the oxide compositions of the cements used elsewhere. The third, the nominal zero-percent- C_3A cement, was from the same lot as the samples used by other investigators in the program.

Paste series from each cement were made at two water/cement ratios, 0.35 and 0.65. Samples of each series were hydrated for periods of 1, 3, 7, 14, 28 and 90 days. The ignition loss of each paste, and the alite and the belite contents were determined.

The pastes were mixed in an evacuated 500 ml brass cylinder which was shaken for 6 minutes in a modified paint-can shaker. The mixes were cast in 1-1/4-in. i.d. polyethylene test tubes, which were then stored at 23.5°C. Each sample was removed from its test tube at the end of its prescribed hydration period. The top and bottom 1/2-in. of the sample were discarded, and the remainder was placed in a vacuum drying apparatus (3). After two or three days of drying, the sample was removed, ground -80 mesh in a controlled atmosphere glove box, and returned to the drying apparatus. Each sample was dried approximately 4 weeks after grinding.

The dried samples were used for X-ray and loss on ignition (1050°C) determinations. Mixtures with silicon for the X-ray work were prepared with a vibratory ball mill, as described by Copeland and Bragg (4).

The X-ray determinations were made using a North American Philips Geiger counter diffractometer and also with a diffractometer incorporating a proportional counter and pulse height analyzer. The radiation was $CuK\alpha$ Ni-filtered. Scanning speed was 1/8° 2 θ per minute.

The X-ray Method

Of the two published alternative methods (1), the procedure involving oxide composition

data cannot be used because the oxide composition of the clinker residue is not known. Hence, the method utilizing only X-ray data must be employed.

Although beyond the scope of the present study, it should be pointed out that the determination of tricalcium aluminate and ferrite phase residues in partly hydrated portland cement pastes cannot be made directly on the paste. X-ray lines from the hydration products interfere with the lines to be measured. In order for such an analysis to be made, the paste sample must first be freed of calcium hydroxide, as Copeland has done using a selective extraction procedure (2). It would be of greater advantage if the extraction procedure removed the calcium silicate hydrate as well.

When only alite and belite residues are to be determined, as in the present investigation, the paste samples need not be extracted. There is a small overlap of the calcium hydroxide line at $51.6^\circ 2\theta$ with the alite-belite line at $52.8^\circ 2\theta$. This overlap can be corrected geometrically before the $52.8^\circ 2\theta$ is measured.

Silicon was used as an internal standard. In pastes, however, the silicon line at $28.4^\circ 2\theta$ used in cement analysis, is interfered with by calcium hydroxide and calcium silicate hydrate gel lines, and cannot be used. The silicon line at $88^\circ 2\theta$ was employed instead (2).

The equations used for alite-belite determination in cements must be modified for the change in silicon line. The intensity of the $28.4^\circ 2\theta$ silicon line is therefore calculated from the intensity of the $88^\circ 2\theta$ line, using the intensity ratio of these lines as determined from pure silicon samples and from cement-silicon mixtures. The value obtained in the present investigation for $I_{88}/I_{28.4}$ is 0.15. Swanson and Fuyat (5) report a value of 0.17. Apparently each investigator employing this method should determine the ratio $I_{88}/I_{28.4}$ with the same equipment as used for the analysis.

The quantity of silicon used in the present application was 15 percent by weight of the paste. Previously, for cement analysis, 10 percent had been used. The amount was increased for the present purposes in order to obtain a more intense $88^\circ (2\theta)$ diffraction line.

The quantities obtained by the X-ray method are the weight ratios of alite to silicon, x_1 , and belite to silicon, x_2 . The equations, given below, relating the intensity ratios to these quantities, have been derived previously (1).

$$\frac{x_2}{x_1 + x_2} = w_2 = \frac{-(B_1 + B_2 R_3)}{2(A_1 + A_2 R_3)} + \frac{\sqrt{(B_1 + B_2 R_3)^2 - 4(A_1 + A_2 R_3)(C_1 + C_2 R_3)}}{2(A_1 + A_2 R_3)} \quad (1)$$

$$x_1 + x_2 = - \frac{R_1}{A_2 w_2^2 + B_1 w_2 + C_1} \quad (2)$$

where R_1 is the intensity ratio of the $51.8^\circ 2\theta$ line, $I_{51.8}$, to the $28.4^\circ 2\theta$ silicon line, $I_{28.4}$, or when the $88^\circ 2\theta$ line is used, $0.15 I_{51.8}/I_{88}$; R_3 is the intensity ratio $I_{51.8}/I_{41}$. The quantities A_1 , B_1 , C_1 , A_2 , B_2 and C_2 are constants whose values have been previously determined (1).

The value of w_2 is calculated from equation (1) and is then used in the calculation of $x_1 + x_2$ from equation (2). The quantities x_1 and x_2 can be easily obtained from w_2 and $x_1 + x_2$. The alite and belite contents are finally obtained as the products $P_0 x_1$ and $P_0 x_2$, where P_0 is the quantity of silicon in grams per gram ignited weight of paste. The quantity P_0 is obtained from the original mixture composition and the ignition loss (at 1050°C) of the original paste.

Results and Discussion

The phase compositions of the three cements were determined by the X-ray method (1); the results are given in Table 1.

The results of the paste studies are given in Table 2. The alite and belite contents of the original cements are included in the table (0 days hydration) for comparison.

The experimental error in the reported alite values varies from ± 3 percent (absolute) for the highest values to ± 1 percent for the lowest. The experimental error in the belite values varies from ± 8 percent in the highest values to ± 4 percent in the lowest values. The belite error is larger than the alite error, because the $51.2^\circ 2\theta$ line used in the determination is primarily an alite line and contains only a weak belite component. The experimental error can be reduced by any means that will increase the number of X-ray counts measured in the determination, such as more scans, or slower scanning, or by extraction of the calcium hydroxide from the paste, which leaves a

Table 1. Compositions of the original cements.

Cement	Normal	White	Nominal O% - C ₃ A
Oxides, percent			
SiO ₂	20.0	24.8	21.5
Al ₂ O ₃	5.28	3.28	3.02
Fe ₂ O ₃	2.50	0.33	6.04
CaO	63.9	66.2	65.2
MgO	2.9	1.4	0.8
MnO	0.47	0.02	0.04
SO ₃	2.4	2.4	2.0
Alkali	0.20	0.16	0.37
Fineness, cm ² /g Blaine	3130	2770	3020
Compounds (XR Method)			
Ferrite, molar A/F	1.02	1.36	0.43
percent	9.2	1.2	13.9
C ₃ A, percent	5.7	5.1	1.4
Alite, percent	57.8	50.8	67.2
Belite, percent	19.5	40.0	13.7

Table 2. Ignition losses and alite and belite residues in partly hydrated cement pastes.

Cement Paste Age days	Normal			White			Nominal O% - C ₃ A		
	Ign. Loss % ign.wt.	Alite % ign.wt.	Belite % ign.wt.	Ign. Loss % ign.wt.	Alite % ign.wt.	Belite % ign.wt.	Ign. Loss % ign.wt.	Alite % ign.wt.	Belite % ign.wt.
	0.35 w/c pastes								
0		57.8	19.5		50.8	40.0		67.2	13.7
1	6.7	37.5	16.2	5.3	32.0	35.3	6.9	41.6	11.2
3	10.3	28.5	18.1	9.0	21.1	32.8	10.5	25.0	9.7
7	12.7	18.6	13.7	11.5	12.3	29.1	12.2	20.7	8.8
14	14.6	15.8	12.1	13.3	7.8	29.3	13.1	16.2	8.1
28	15.8	11.8	7.1	14.3	8.8	21.4	14.3	12.9	7.3
90	17.7	9.2	2.8	15.8	6.2	15.4	15.4	9.4	5.5
	0.65 w/c pastes								
0		57.8	19.5		50.8	40.0		67.2	13.7
1	7.0	37.9	17.0	6.2	29.7	35.2	7.7	34.1	11.0
3	11.1	23.4	12.2	10.2	15.1	31.2	11.1	22.4	6.3
7	14.3	15.7	12.0	12.1	9.6	27.9	12.9	17.0	7.6
14	17.0	11.4	8.4	13.2	6.9	25.9	14.2	12.6	6.4
28	18.3	7.1	6.9	15.0	5.1	24.0	15.2	3.2	11.2
90	20.7	3.4	1.2	17.2	7.8	7.9	18.3	4.0	4.4

Figure 1. Degree of hydration versus time, alite and belite phases, normal portland cement.

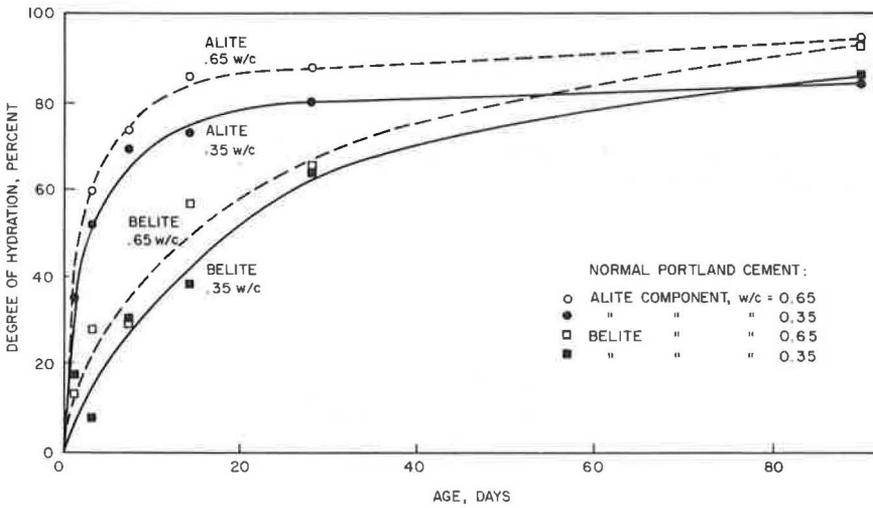


Figure 2. Degree of hydration versus time, alite and belite phases, white portland cement.

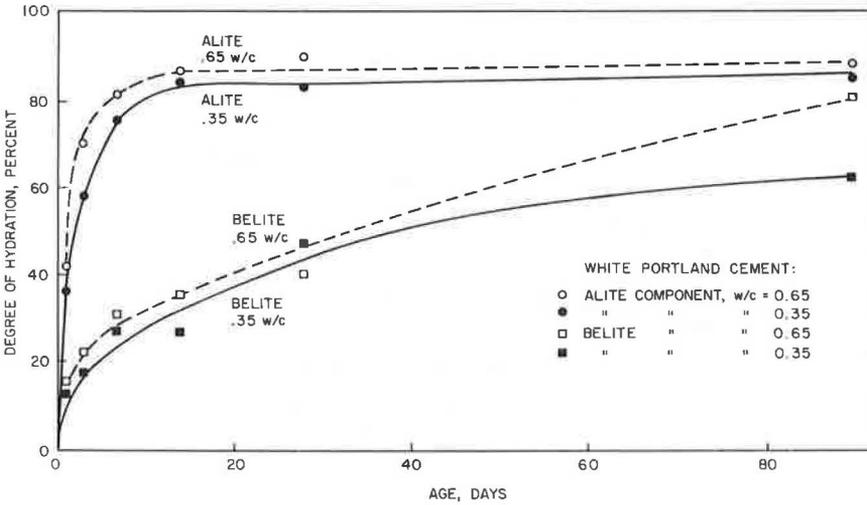


Figure 3. Degree of hydration versus time, alite and belite phases, zero percent C₃A.

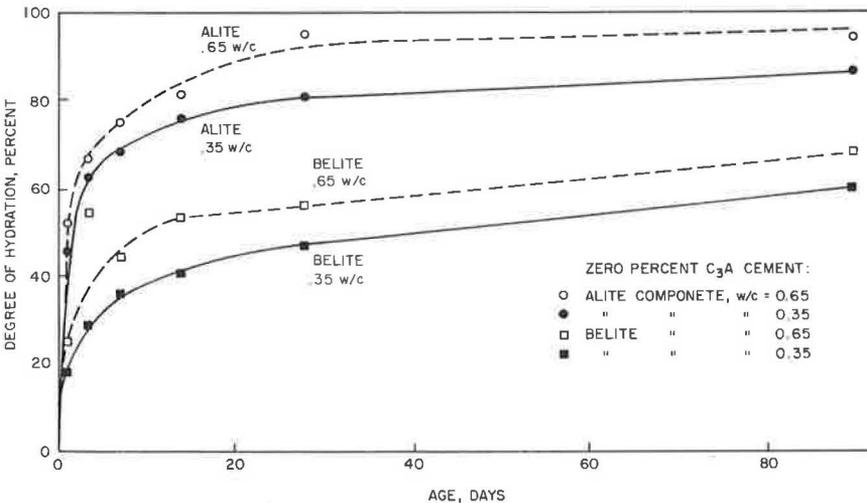


Figure 4. Degree of hydration versus time, alite phase, three different cements.

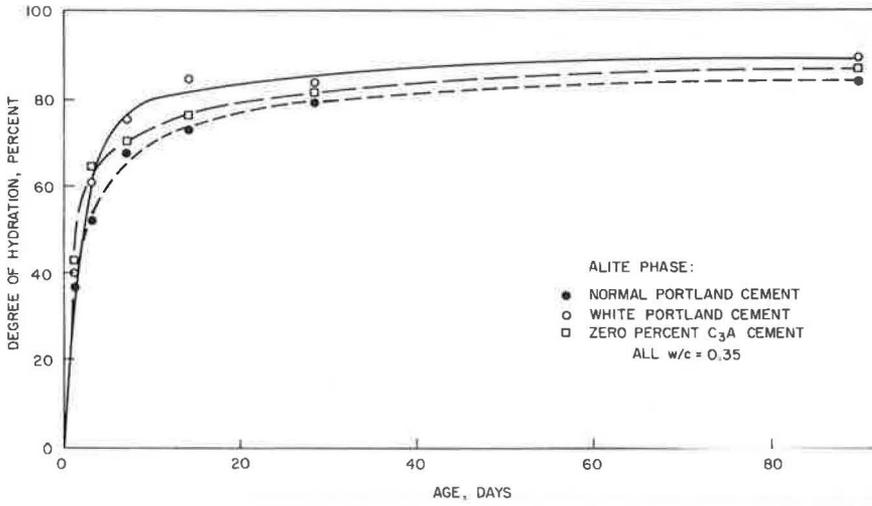
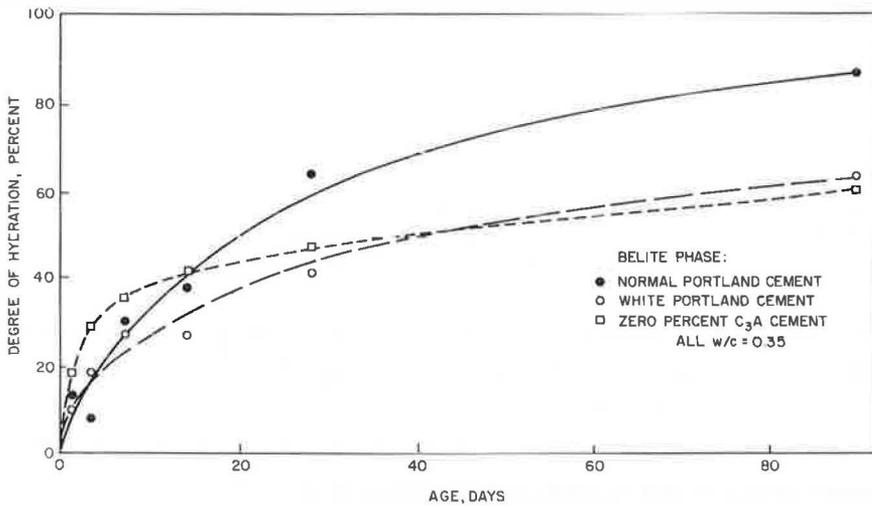


Figure 5. Degree of hydration versus time, belite phase, three different cements.



residue enriched with respect to the unhydrated components.

The degree of hydration of alite and belite in the various pastes, as a percentage of the quantity originally present, can be obtained from the data in Table 2. The values are plotted as functions of time in Figs. 1, 2, and 3.

The effect of water/cement ratio on the degree of hydration can be seen in Figs. 1, 2, and 3. For all three cements, at any given paste age, the degree of hydration is lower at the lower water/cement ratio.

The slower hydration of belite, relative to alite, is shown by the curves. This effect, as well as the water/cement ratio effect, is clear, in spite of the relatively large experimental error in the belite determination.

For the three cements used in the present investigation the alite contents vary from 50 to 67 percent and the belite contents vary from 13 to 40 percent in the unhydrated materials. One cement has practically no C_3A while another has no ferrite phase. The alite and belite hydration data have been compared for any gross differences between cements. The data for the degree of hydration of alite for the three 0.35 w/c series are plotted as functions of time in Fig. 4. The differences among the three curves are small. The white cement curve is slightly higher, although the white cement was of slightly lower fineness (Table I). Whether the higher percentage of alite hydration is related to the absence of iron in the system or is the result of the lower initial content cannot be determined from these data.

The results for the degree of hydration of belite for the three 0.35 w/c series are plotted as functions of time in Fig. 5. At relatively early ages, up to 14 days, there is some correlation between degree of hydration at a given time and initial belite content. At later ages, a significantly greater fraction of the belite has hydrated in the normal portland cement case than in the other two. At the higher w/c ratio, however, both the normal and white cement belite have hydrated to a greater extent than the belite in the zero- C_3A cement.

The results presented here illustrate an application of X-ray diffraction to the study of hydrated pastes. The method has several useful functions. It is being used as a research tool to determine the influence of cement composition and other variables on the rates of hydration of alite and belite. The X-ray method may also prove useful in explaining unusual hydration characteristics when encountered.

Summary

The alite and belite contents of the clinker residue of partly hydrated cement pastes can be obtained by X-ray quantitative analysis.

The X-ray method used is essentially the same as that for unhydrated cements.

The results of determinations on pastes from three different portland cements demonstrates the increase in hydration both of alite and belite at any given time with increase in the water/cement ratio.

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EXAMINATION OF CEMENT PASTES, HYDRATED PHASES, AND SYNTHETIC PRODUCTS BY X-RAY DIFFRACTION

Katharine Mather, U.S.A.E. Waterways Experiment Station

Introduction

One of the techniques used to identify hydration products in cement pastes, hydrated phases, and synthetic products was X-ray diffraction. X-ray diffraction has been