

# Factors Influencing Cessation of Hydration in Water Cured Cement Pastes

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This paper includes a presentation of new experimental data together with an analysis of previously published data bearing on the conditions under which hydration of continuously water cured cement paste may cease. Empirical equations, which allow prediction of the end-point of hydration, are derived and the implications of limiting hydration on the relation between strength and the gel-space ratio are discussed.

•IT IS well known that hardened concrete, even after prolonged immersion in water, contains appreciable quantities of unhydrated cement. When curing is limited, as is usually the case in service, 50 percent or more of the original cement may never be hydrated and serves only as expensive aggregate. Apart from the obvious economic implications, restriction of hydration and the conditions under which complete hydration might be achieved are important factors relevant to any study of the process whereby cement hydrate is formed and deposited within the boundaries of space originally occupied by mixing water.

Although many writers (1, 2, 3, 4) had published evidence of the interdependence of water/cement ratio and the rate of hydration, it was Powers (1, 5) who, at the time of starting the present work, had advanced the most rational explanation of the phenomenon of limiting hydration. In his earlier work Powers suggested that in dense cement pastes hydration stopped when the space originally occupied by mixing water became filled with the bulked products of hydration. Adsorption studies had indicated that pore space remaining at this stage was of molecular dimensions and that the total quantity of water contained therein amounted to, at most, four monolayers capacity. It was possible, therefore, to argue that hydration would be inhibited by one or both of the following causes: (a) lack of space capable of accommodating new solids formed in the hydration process; or (b) the extremely slow rate of diffusion of water through the porous hydrate due, first, to the inherently low permeability of this material and, second, to a large increase in the effective viscosity of such water arising from the action of adsorption forces.

In a later paper, Powers (6) reported data concerning a particular cement in which it appeared that complete hydration was possible for all water/cement ratios greater than a critical value giving, at the same time, minimum porosity and complete hydration of the cement.

At that time, however, the author had reason to doubt whether complete hydration was possible in a hardened cement paste. Study of the literature confirmed that the time taken to reach both limiting hydration and the ultimate degree of hydration depended upon the water/cement ratio, but there was generally no proof that complete hydration had in fact been achieved.

Reappraisal of Powers' earlier work suggested that, contrary to the indications of his recent publication (6), the ratio  $w_e/w_n w_0$  (a list of symbols is given in the Appendix of this paper;  $w_n$  is proportional to the amount of cement hydrated) at cessation of hydration was very nearly constant for cements having nearly the same  $C_3A$  content. The linear relationship between  $w_e/w_n$  and  $w_0$  for cements having a  $C_3A$  content of about 6 percent was also found to fit the data of Czernin (10) and Verbeck and Foster (9) with

fair accuracy. The author was, however, unable to advance any convincing physical explanation for the linear relationship between  $w_e/w_n$  and  $w_o$ .

In view of the unresolved inconsistencies in the literature it was thought necessary to embark on further experimental work. It was considered necessary to supplement observations on hardened paste and mortars with tests in which cement was continuously ball-milled in an excess of water until complete hydration was achieved.

## METHODS OF ESTIMATING THE DEGREE OF HYDRATION

### The Determination of $w_n$ , $w_e$ and $w_t$

The new solid formed when unit weight of cement is completely hydrated contains a weight of chemically bound water which should be characteristic of the cement studied. A saturated cement paste also contains water which is strongly adsorbed onto the surface of cement hydrate and water which is contained in relatively coarse capillary pores. The three different categories of water are classified according to the ease with which they may be evaporated from the solid.

Capillary water which can be relatively easily separated from the solid at room temperatures is usually regarded as the water lost when the relative humidity in the pores is depressed to 45 percent. At this stage the least dimension of pores containing the remaining free water is probably less than 20 Å and the hydraulic tension in the water is about 1100 atmospheres. (6).

The remaining free water, the gel water, is usually taken as that which is evaporated when the relative humidity in the pores is depressed from 45 percent to zero. Some difficulty arises in the definition of the end point and here, consequently, an arbitrary classification has to be made. In this paper the end point is defined as that corresponding to oven-drying at 110 C. Under such conditions the remaining water, called the nonevaporable water, is about 89 percent of the nonevaporable water obtained by drying at room temperature over magnesium perchlorate and about 97 percent of the nonevaporable water obtained by drying under high vacuum by the dry-ice method.

The nonevaporable water  $w_n$  is taken to be that part of the total water content which is lost when the specimen, which has been brought to the "bare surface" condition by one of the above drying methods, is ignited at 1000 C.

The oven-drying method has the merit of simplicity and can be used with large solid samples; it has the disadvantage that part of the chemically bound water, particularly on samples having high  $C_3A$  contents, is lost.

Since most of the tests in this program were carried out on large samples, the oven-drying technique was used throughout and the nonevaporable water  $w_n$  is herein defined as the water per unit weight of anhydrous cement which is held at 110 C and lost on ignition at 1000 C. Where it has been necessary to compare the writer's results with those of other workers using the magnesium perchlorate method, a factor of 0.89 has been applied to the  $w_n$  values obtained by the latter method and the values of evaporable water  $w_e$  adjusted by the difference between the two values of  $w_n$ , the total water  $w_t$  remaining the same in both cases.

### Basic Equations

Supposing that when unit weight of cement is fully hydrated, the nonevaporable water content is  $w_n^0$  and that when a weight fraction  $\alpha$  has been hydrated the nonevaporable water is  $w_n$ , the degree of hydration is defined as  $\alpha = w_n/w_n^0$ . The total water at any stage of hydration is then given by

$$w_t = w_o + \frac{\alpha w_n^0}{k} \quad (1)$$

and the evaporable water is given by

$$w_e = w_o - \alpha w_n^0 \left(1 - \frac{1}{k}\right) \quad (2)$$

where the quantity,  $\alpha w_n^0/k$  is the weight of water per unit weight of cement which must be supplied from an external source in order to maintain the paste in a saturated condition.

### Practical Difficulties

In conditions where it can be insured that all the pores of the solid remain filled with water and the quantities  $w_t$ ,  $w_e$  and  $w_n$  are determined by weighing, the term  $\alpha w_n^0 [1-(1/k)]$  may be taken as the reduction in specific volume resulting from the combination of  $\alpha$  grams of cement and  $\alpha w_n^0$  grams of water. This may not be strictly correct since some of the evaporable water is likely to be highly compressed (7). When the cement is hydrated by continuous ball-milling, compression of any part of the free water would seem unlikely for the following reasons: (a) it was observed in this experiment that when hydration had slowed down to a negligible rate, the slurry became progressively more viscous; and (b) since this effect was not associated with any substantial hydration it was concluded that the structure of the gel was being broken up and dispersed in the slurry. Under such circumstances, therefore, the term  $\alpha w_n^0 [1-(1/k)]$  is considered to be an accurate measure of the reduction in specific volume resulting from the complete reaction of  $\alpha$  grams of cement with  $\alpha w_n^0$  grams of water.

Estimation of the volume available to accommodate cement hydrate in solid samples is likely to be in error when the quantities  $w_n$ ,  $w_e$  and  $w_t$  are determined by weighing. Apart from the difficulty in establishing  $w_t$  accurately for a surface-wet sample, the value of  $w_e$  is likely to be affected by self-desiccation. This is clearly demonstrated in Powers' earlier work (1, pp. 859-863) since values of  $k$  estimated from weight analyses of his samples are subject to large variations and are in any case very different from the corresponding  $k$  values determined by helium displacement (1, p. 694).

For the reasons mentioned, accurate estimation of the parameters defining pore space was considered essential to the success of the investigation. Since this could not be achieved by simple transformation of observed weight losses, other means had to be sought. The helium displacement method of Powers was rejected on practical grounds and also because there is ample evidence (6, 8) to show that water is able to occupy space in the fine pores of cement hydrate which cannot be penetrated by other fluids and gases. It was decided that this difficulty could be overcome by direct measurement of  $k$  if ball-milling of the cements could be done in suitable closed vessels capable of serving as pycnometers. The experiments therefore fell into two categories: (a) determination of the constants  $w_n^0$  and  $k$  for each cement by means of continuous ball-milling in pycnometer bottles, and (b) tracing the course of hydration in hardened samples by direct observation of  $w_n$  using the oven-drying method.

## EXPERIMENTAL

### Materials

Essential properties of the materials used and details of the mixes are presented in Tables 1, 2 and 3.

### Ball-Milled Slurries

The ball-milled samples were prepared in bottles of about  $\frac{1}{2}$ -liter capacity, fitted with ground glass stoppers and charged with glass marbles  $\frac{1}{2}$  in. in diameter. A hole approximately  $\frac{1}{2}$  mm in diameter was drilled to intersect the highest point of the domed inside surface of each stopper. The volume of each bottle was determined by weighing it when filled with de-aired water at 25 C.

Each sample of cement was weighed and placed in the bottle which was then re-weighed. The bottle, marbles and cement were then connected to a vacuum system by means of a rubber suction cup and a T-junction, one branch of which was connected to the vacuum system and the other to a reservoir of de-aired tap water. By suitable manipulation of cocks in the three branches of the T-junction, the bottle could be rapidly filled with water to within 5 cc of the top. A hypodermic syringe was used to complete the filling operation. By this means the bottle and its contents, completely

TABLE 1  
PROPERTIES OF MATERIALS

Material	Chemical Composition (% by wt)							Calculated Compounds (% by wt)				Fineness (cm <sup>2</sup> /gm Blaine)
	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>		C <sub>2</sub> S	C <sub>3</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	
Portland cement, OP	22.5	2.5	5.6	65.8	1.3	1.6		25.6	49.7	10.6	7.6	2740
Portland cement, RP	22.2	2.6	5.8	65.6	1.2	1.9		26.0	48.4	10.9	7.9	3230
Blast-furnace slag, S	32.9	0.7	16.1	30.6	20.0	0		—	—	—	—	3810
Milled quartzite, Q	98.7	—	—	0	—	—		—	—	—	—	4000

free of air bubbles, could be weighed within 30 sec of admitting water. At this stage hydration was considered to be zero.

After filling, the bottle was sealed with a strip of adhesive tape and attached by means of spring clips to a wheel capable of rotating in the vertical plane. The longitudinal axis of each bottle lay along a radius of the wheel and agitation of the bottle and its contents was accomplished by rotating the wheel at a rate of about 1 revolution per sec.

From time to time the bottles were removed and allowed to stand until clear water appeared at the top. The adhesive tape was then stripped, this process being usually accompanied by an audible hiss as air entered the bottle. The air bubble appearing below the hole in the stopper was filled by means of a hypodermic syringe and the bottle was then re-weighed. The end point of hydration was assumed to have been reached when there was no detectable difference in the weight of a bottle after a period of two weeks continuous milling. It was usually found necessary to continue the milling process for about two months before the end point was reached.

At the end of the milling period samples were oven-dried and ignited to determine  $w_e$  and  $w_n$ . The weight of water taken up during this process,  $\Delta w$ , was then used to calculate  $k$  from the relation

$$\frac{w_n}{\Delta w} = k \quad (3)$$

The balance of the mix was diluted to a water/cement ratio of about 12 and stored for other tests such as X-ray and adsorption studies. After about one year of storage it was found that the value of  $w_n$  had increased slightly and this final value was assumed to be  $w_n^0$ .

#### Solid Mortars

Specimens of hardened mortar with initial water/cement ratios ranging from 0.25 to 0.85 were cast in the form of 2-in. cubes in batches of 72 for each mix. Loss of water due to bleeding was prevented by adding to each mix appropriate quantities of siliceous rock flour ground to cement fineness. All mixes were extremely stiff pastes and were compacted by heavy vibration.

TABLE 2

DETAILS OF MIXES FOR 2-INCH CUBES

Mix	Weight Proportions of Materials			
	OP	S	Q	Water
PC.25	1	—	0	0.25
PC.30	1	—	0.17	0.30
PC.35	1	—	0.34	0.35
PC.40	1	—	0.52	0.40
PC.45	1	—	0.69	0.45
PC.55	1	—	1.03	0.55
PC.65	1	—	1.38	0.65
PC.75	1	—	1.75	0.75
PC.85	1	—	2.06	0.85
PS1.22	0.5	0.5	0	0.22
PS1.30	0.5	0.5	0.17	0.30
PS1.45	0.5	0.5	0.69	0.45
PS1.55	0.5	0.5	1.03	0.55
PS1.65	0.5	0.5	1.38	0.65
PS2.45	0.75	0.25	0.69	0.45
PS3.45	0.25	0.75	0.69	0.45

TABLE 3

MIX PROPORTIONS OF SLURRIES FOR BALL-MILLED SAMPLES

Mix	Weight Proportions of Materials			
	OP	RP	S	Water
SOP1	1.00	—	—	2.127
SOP2	1.00	—	—	2.130
SOP3	1.00	—	—	2.128
SOP4	1.00	—	—	4.700
SOP5	1.00	—	—	4.680
SOP6	1.00	—	—	4.698
SRP7	—	1.00	—	2.170
SPS1	0.50	—	0.50	2.178
SPS2	0.50	—	0.50	2.683
SPS3	0.50	—	0.50	2.118
SPS4	0.50	—	0.50	4.665
SPS5	0.50	—	0.50	4.710
SPS6	0.50	—	0.50	4.605
SPS7	0.75	—	0.25	4.650
SPS8	0.25	—	0.75	4.645
SPS9	0.10	—	0.90	4.691

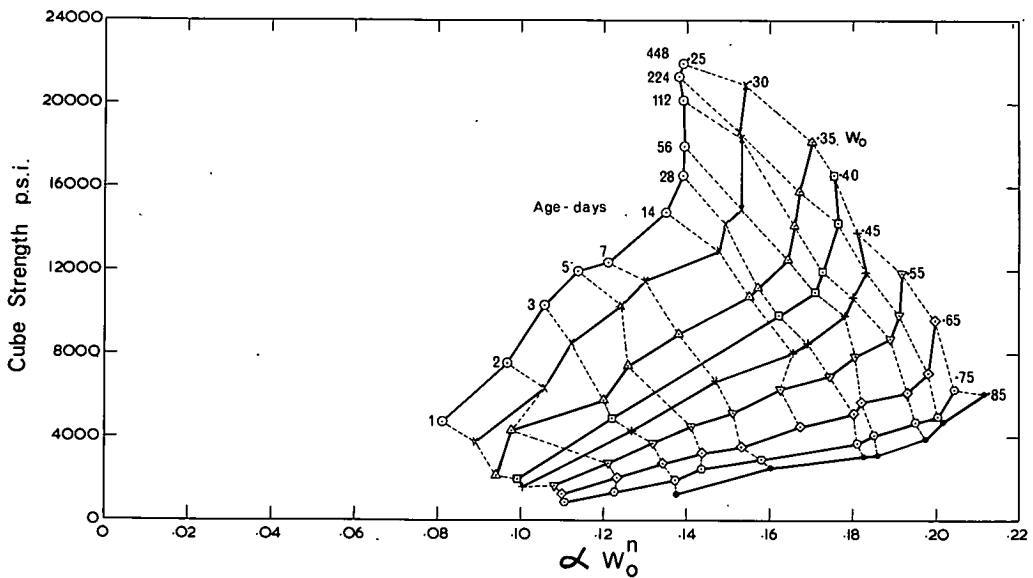


Figure 1. Observed values of cube strength and nonevaporable water for various ages and water/cement ratios for portland cement OPI.

At various ages groups of five cubes from each mix were crushed in order to determine compressive strength, and the debris was analyzed in order to determine  $w_n$ . For the purpose of determining the true values of  $w_e$  and  $w_t$  the value of  $k$  obtained in Eq. 3 was used. The value of  $k$  obtained from the ratio of nonevaporable water to the difference between total water and original water per unit weight of cement as determined by weighing was about 35 percent lower than that obtained by means of Eq. 3. The lower value for  $k$  obtained from the mortars was ascribed to self-desiccation in the solid samples and thus values obtained from bottle-hydrated samples were preferred.

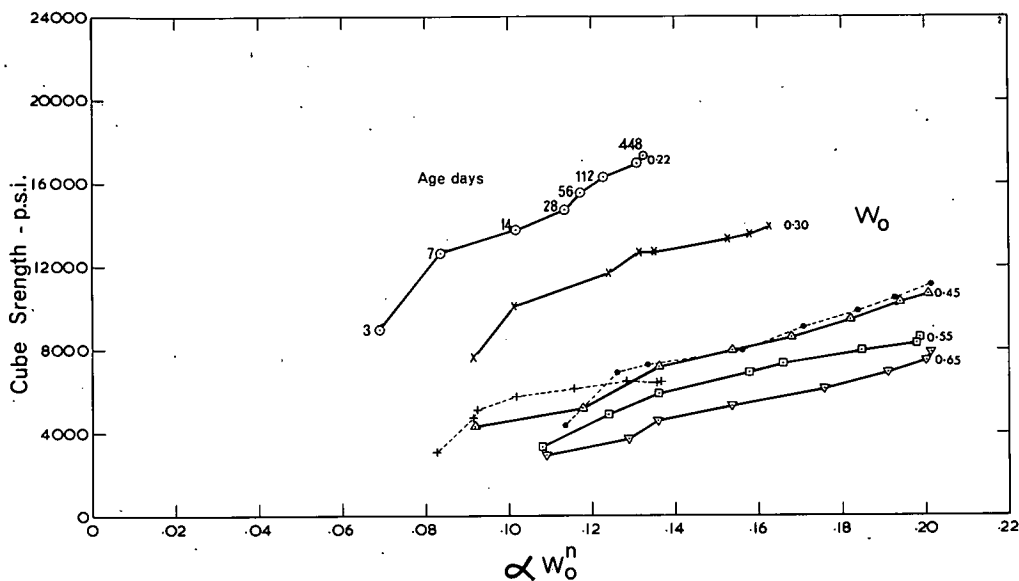


Figure 2. Observed values of cube strength and nonevaporable water for various ages and water/cement ratios for 50/50 mixtures of portland cement and blast-furnace slag; the broken lines are for 75/25 and 25/75 mixtures with water/cement ratio = 0.45.

## RESULTS

### Hardened Pastes

Corresponding determinations of strength and nonevaporable water are shown in Figure 1 for mixes containing only portland cement and in Figures 2 and 3 for mixes in which portland cement was mixed with blast-furnace slag. Relationships between hydration factor  $\alpha$  and age for the various mixes are shown in Figures 4, 5 and 6. It will be noted that certain mixes were not tested at early and intermediate ages; this was due to practical difficulties concerning equipment. All mixes were, however, tested at 56, 112, 224 and 448 days.

Each point on Figures 1, 2 and 3 is the mean of at least four, and usually five, cube crushing tests. The quantity  $\alpha w_n^0$  was determined by the oven-drying technique on samples weighing about 70 gm. Within each group the standard deviation of the cube strength ranged from 160 psi in weak mixes at early ages to 520 psi in strong mixes at 448 days. The standard deviation for values of  $\alpha w_n^0$  was approximately constant and had a mean value of 0.009 for all results.

Values of  $\alpha w_n^0$  and the cube strength  $\sigma$  at the age of 448 days are tabulated in Table 4 together with various derived quantities to be discussed later in this report.

### Ball-Milled Slurries

As mentioned previously, it was found necessary to effect considerable dilution of the original slurries in order to obtain complete hydration of the cement. This was particularly the case with initial water/cement ratios of about 2. After a milling period of about 35 days, the slurry became extremely viscous and the movement of the glass spheres became so slow as to render the grinding action ineffective. At this stage it was virtually impossible to eliminate air bubbles or to get clear water at the top of the suspension. When this stage was reached, the test at the particular water/cement ratio was terminated, the bottle was emptied of its contents and the slurry was diluted.

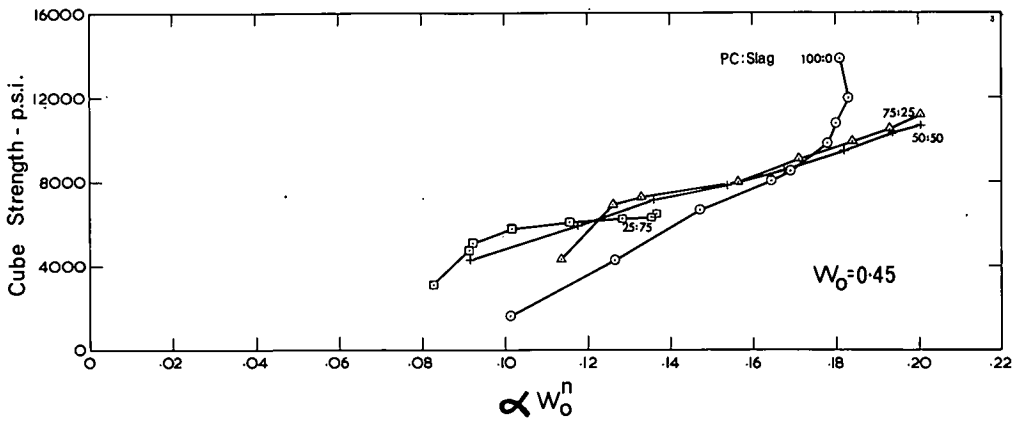


Figure 3. Observed values of cube strength and nonevaporable water for various proportions of portland cement and blast-furnace slag; the water/cement ratio was 0.45 for all mixes.

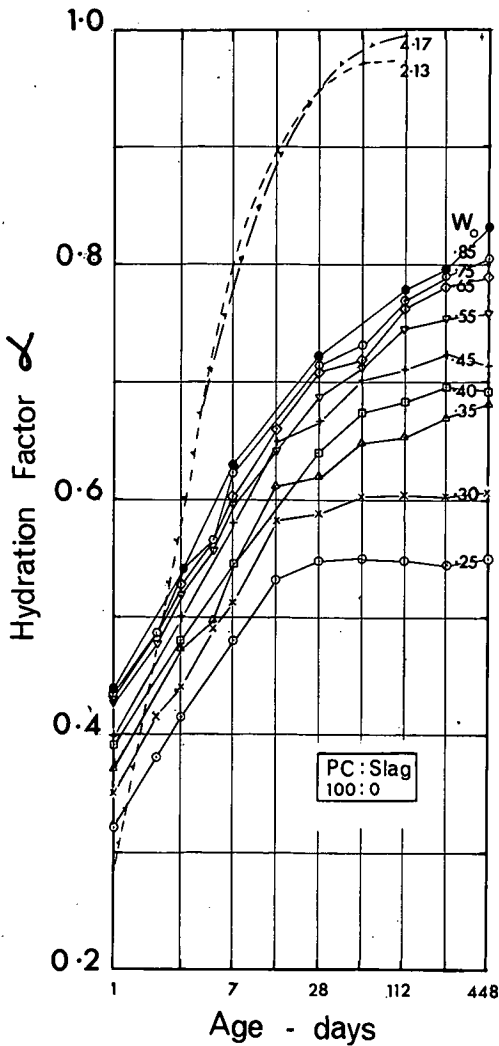


Figure 4. Variation of hydration factor  $\alpha$  with age for portland cement pastes having various values of water/cement ratio.

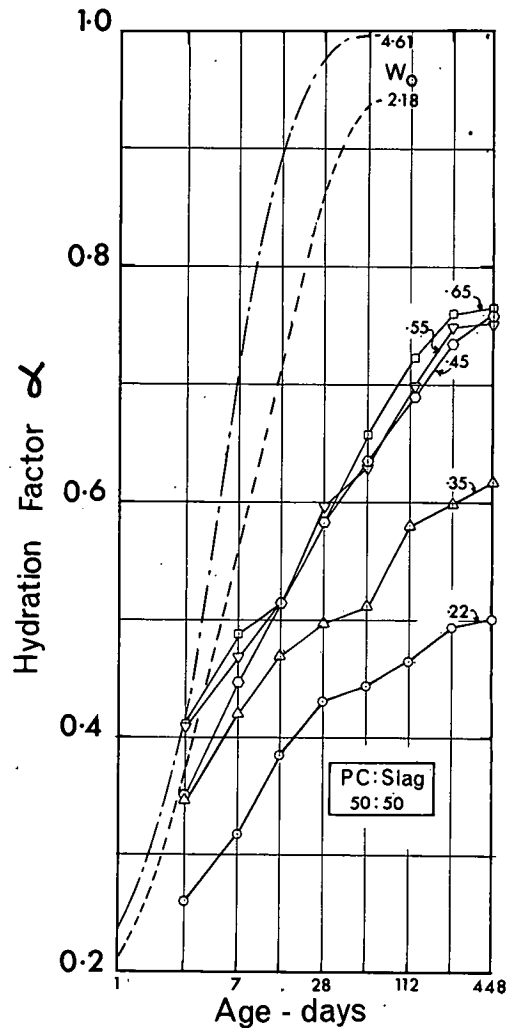


Figure 5. Variation of hydration factor  $\alpha$  with age for 50/50 mixtures of portland cement and blast-furnace slag having various values of water/cement ratio.

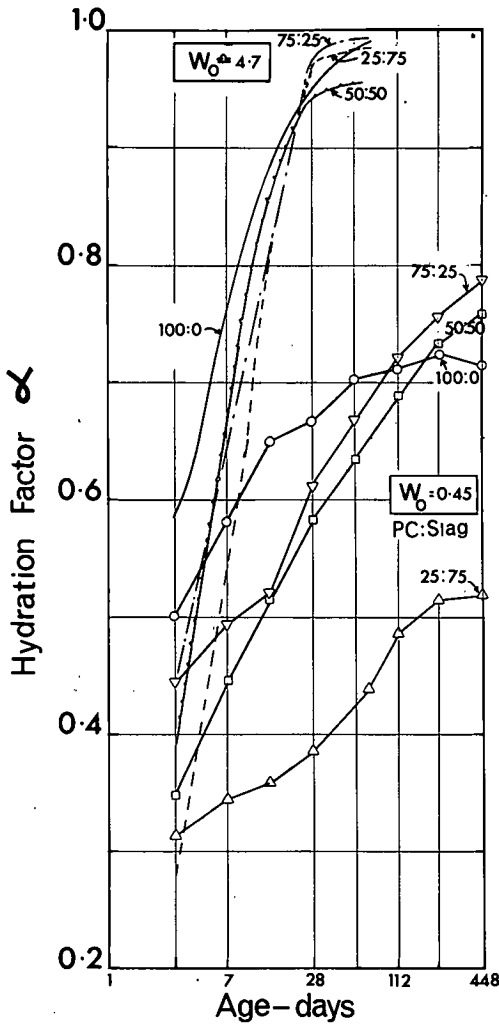


Figure 6. Variation of hydration factor  $\alpha$  with age for pastes having various proportions of portland cement and blast-furnace slag; the slurry mixes had water/cement ratios of approximately 4.7 and the mortar mixes had a water/cement ratio of 0.45.

TABLE 4  
RESULTS OF TESTS ON SOLID SPECIMENS AT 448 DAYS

Cement OP/S	Mix	$\alpha$	$\sigma$	$\frac{w_e}{w_n}$	$\frac{w_e}{w_n w_o}$	$V_{hc}$ (Eq. 4)	$V_{uc}$ (Eq. 5)	C (Eq. 6)	$A_c$ (Eq. 9)
100/0	PC. 25	0.549	21,920	1.057	4.24	0.461	0.236	0.651	0.146
	PC. 30	0.608	20,830	1.207	4.03	0.511	0.205	0.620	0.146
	PC. 35	0.671	18,110	1.317	3.76	0.564	0.172	0.599	0.137
	PC. 40	0.692	16,550	1.542	3.86	0.582	0.161	0.561	0.145
	PC. 45	0.715	13,800	1.745	3.88	0.601	0.149	0.530	0.149
	PC. 55	0.758	11,980	2.125	3.86	0.637	0.127	0.481	0.149
	PC. 65	0.789	9,600	2.512	3.86	0.663	0.110	0.439	0.149
	PC. 75	0.806	6,270	2.935	3.91	0.677	0.101	0.402	0.152
	PC. 85	0.833	6,020	3.291	3.88	0.700	0.087	0.374	0.145
50/50	PS1. 22	0.501	17,370	0.986	4.49	0.407	0.261	0.659	0.152
	PS1. 30	0.617	13,900	1.164	3.88	0.502	0.201	0.620	0.143
	PS1. 45	0.759	10,620	1.568	3.49	0.617	0.126	0.548	0.128
	PS1. 55	0.752	8,600	2.091	3.80	0.612	0.130	0.477	0.153
	PS1. 65	0.765	7,920	2.539	3.90	0.622	0.123	0.428	0.164
75/25	PS2. 45	0.789	11,110	1.529	3.40	0.649	0.110	0.560	0.113
	PS3. 45	0.518	6,410	2.656	5.90	0.409	0.252	0.415	0.272

Note:  $\alpha$ ,  $w_e/w_n$ ,  $w_e/w_n w_o$ , C and  $A_c$  are nondimensional;  $V_{hc}$  and  $V_{uc}$  are in units of volume and take their dimension from the unit chosen for the diameter of the basic spherical particle having diameter = 1 unit.



TABLE 5  
TEST RESULTS AND CALCULATED VALUES FOR BALL-MILLED SLURRIES

Mix	Mean Values			At Termination of Test				
	$w_n^0$	g	$k^*$	$\alpha$	$k^{**}$	$\frac{w_e}{w_n}$	C	$A_c$
SOP1				0.972	3.90	7.91	0.199	0.091
SOP2				0.969	3.78	7.94	0.199	0.097
SOP3				0.927	3.80	8.29	0.192	0.174
SOP4	0.253	3.22	3.87	0.980	3.88	18.21	0.098	0.073
SOP4				0.998	3.88	17.79	0.100	0.016
SOP6				0.992	3.92	17.98	0.099	0.039
SRP7				0.929	3.80	8.44	0.189	0.170
SPS1				0.940	3.19	7.80	0.199	0.152
SPS2				0.898	3.00	10.30	0.153	0.217
SPS3				0.897	3.12	8.30	0.192	0.220
SPS4	0.261	3.09	3.10	0.957	2.99	17.24	0.097	0.122
SPS5				0.992	3.08	17.24	0.103	0.039
SPS6				0.996	3.07	16.31	0.106	0.024
SPS7	0.255	3.16	3.42	0.992	3.42	17.64	0.101	0.039
SPS8	0.264	3.03	2.71	0.984	2.71	17.12	0.104	0.061
SPS9	0.239	2.910	2.34	0.903	2.37	18.85	0.096	0.210

\*Mean of all observations including those at intermediate stages of hydration.

\*\*Values corresponding to  $\alpha$ .

$$\text{Note: } \frac{w_e}{w_n} = \frac{w_o}{\alpha w_n^0} \left( 1 - \frac{1}{k} \right)$$

$$C = \frac{\alpha \left[ 1 + g w_n^0 \left( 1 - \frac{1}{k} \right) \right]}{\alpha + w_o g}$$

$$A_c = (1 - \alpha)^{2/3} \quad (\text{for ball-milled slurries, } A_c = A/\pi)$$

The end point of hydration was taken as given by the nonevaporable water content of the dilute slurry after storage for about 1 year. The end point of the test at the designated water/cement ratio was taken as given by the nonevaporable water content at the end of the milling operation.

The results of tests on ball-milled samples are given in Table 5 together with calculated values of various parameters referred to later in the discussion. The nonevaporable water contents at ultimate hydration are also given in Table 5, each value being the mean of three determinations.

Some of the results of tests on slurries are included in Figures 4, 5 and 6 for easy comparison with the results of tests on hardened samples containing the same cement. These results appear at first sight to be anomalous since at early ages the rate of hydration of hardened pastes and mortars is greater than that of the slurries. This is explained by the fact that larger samples of hardened material weighing about 70 gm took about two weeks to reach constant weight at 110 C, whereas the slurry samples containing only about 1/2 gm solid material reached constant weight after only a few days at 110 C. At early ages, therefore, the  $w_n$  values of both types of sample were probably incorrect and the discrepancy in the case of solid samples was much greater than that encountered with slurries.

## CALCULATIONS

The Quantities  $w_n^0$ ,  $\alpha w_n^0$ ,  $\alpha$ ,  $w_e$  and  $w_e/w_n$ 

Calculation of these quantities was based on the assumption that the  $k$  values obtained in the tests of cement slurries were correct and that the  $w_t$  values obtained by weighing were probably in error. The quantities  $w_n^0$ ,  $\alpha w_n^0$ ,  $\alpha$ ,  $w_e$  and  $w_e/w_n$  were therefore calculated from Eqs. 1, 2 and 3 using the nominal values of  $w_0$  and observed values of  $\alpha w_n^0$  and  $k$ .

The Geometrical Parameters  $V_{hc}$ ,  $V_{uc}$ ,  $C$  and  $A_c$ 

Considering an ideal cement composed of uniform size spherical grains of unit diameter, the following equations are applicable: the absolute volume of hydrated cement produced by each grain,

$$V_{hc} = 0.5236 \alpha \left[ 1 + g w_n^0 \left( 1 - \frac{1}{k} \right) \right] \quad (4)$$

the absolute volume of the unhydrated nucleus of each grain,

$$V_{uc} = 0.5236 (1 - \alpha) \quad (5)$$

the volume concentration of solid hydrated cement in the space surrounding the unhydrated nucleus,

$$C = \frac{\alpha \left[ 1 + g w_n^0 \left( 1 - \frac{1}{k} \right) \right]}{\alpha + w_0 g} \quad (6)$$

and the surface area of the unhydrated nucleus,

$$A = \pi (1 - \alpha)^{2/3} \quad (7)$$

On the assumptions that cement hydrate grows outwards from the unhydrated nucleus of each grain and that the area of voids cut by any plane in space outside the nucleus is a statistically uniform proportion of the total area on the plane, the area concentration of water on the surface of the unhydrated nucleus is

$$A_u = 1 - C^{2/3} \quad (8)$$

The area of contact between water and active cement may therefore be expressed as a dimensionless fraction of the surface area of the cement before it was mixed with water:

$$A_c = (1 - \alpha)^{2/3} (1 - C^{2/3}) \quad (9)$$

In the present investigation  $k$ ,  $g$  and  $w_n^0$  were obtained by weight analyses of slurry samples which were ball-milled in pycnometer bottles. Values of  $w_n = \alpha w_n^0$  were obtained by weight analysis of the solid specimens.

Where comparisons were made with Powers' early results (1) a factor of 0.89 was applied to the published values of  $w_n$ , and values of  $k$  based on helium displacement were used without modification.

TABLE 6  
CHARACTERISTICS OF CEMENTS USED IN PREVIOUSLY PUBLISHED WORK

Source	Cement	Compound Composition (percent)					Constants		
		C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	CaSO <sub>4</sub>	g	w <sub>n</sub> <sup>o</sup>	k
Powers (1)	14930	22.7	55.8	6.1	9.8	2.6	3.22	0.253	3.59
	15007	48.0	29.1	6.8	10.5	2.2	3.19	0.253	3.59
	15011	45.1	29.1	6.7	10.5	2.4	3.20	0.253	3.59
	15013	39.0	29.0	14.0	7.0	3.0	3.16	0.253	3.59
Verbeck and Foster (9)	II	40.9	34.4	5.6	12.9	—	3.22	0.253	3.87
	IV	25.2	51.5	4.8	11.6	—	3.22	0.253	3.87
	V	41.0	39.0	3.7	10.0	—	3.22	0.253	3.87
	I	49.6	24.5	11.0	8.0	—	3.22	0.253	3.87
	III	59.2	14.1	9.3	7.9	—	3.22	0.253	3.87

TABLE 7  
VALUES OF GEOMETRICAL PARAMETERS FOR  
PREVIOUSLY PUBLISHED WORK

Source	Cement	Age (days)	w <sub>o</sub>	$\frac{w_e}{w_n}$	A <sub>c</sub>
Powers (1)	14930	447	0.311	1.212	0.136
		362	0.443	1.752	0.152
		365	0.573	2.291	0.169
	15007	480	0.344	1.229	0.123
		440	0.464	1.684	0.128
		440	0.595	2.156	0.124
	15011	478	0.319	1.227	0.135
		368	0.442	1.639	0.134
		368	0.595	2.291	0.145
	15013	339	0.332	0.990	0.087
		333	0.453	1.392	0.084
		333	0.599	1.943	0.084
Verbeck and Foster (9)	II	2,370	0.400	1.575	0.151
	IV	2,370	0.400	1.612	0.156
	V	2,370	0.400	1.506	0.140
	I	2,370	0.400	1.265	0.100
	III	2,370	0.400	1.265	0.100
Czernin (10)	(a)	—	0.15	0.61	—
	(b)	—	0.19	0.59	—

Note:  $\frac{w_e}{w_n} = \frac{w_o}{\alpha w_n} - (1 - \frac{1}{k})$

$$A_c = (1 - \alpha)^{2/3} (1 - C^{2/3})$$

In the case of Verbeck and Foster's results (9) there was no means of determining  $k$ ; in this case the authors' value of  $k = 3.87$  was adopted. Here, as in the case of Powers' results, a factor of 0.89 was applied to published values of  $w_n$ . Where it was necessary, a mean value of  $w_n^0 = 0.253$ , as obtained in the author's tests, was assumed. Relevant characteristics of the cements and values of the geometrical parameters calculated on the above basis for such data as were chosen for comparison with the author's results are presented in Tables 6 and 7.

### DISCUSSION

Any appreciation of the data presented herein hinges on two important questions: (a) has a state of complete hydration been achieved and can this state be satisfactorily defined, and (b) in specimens containing both unhydrated cement and chemically free water, has it been proved that further reaction of these components was inhibited under the stated conditions?

Insofar as this investigation, and indeed any similar investigation known to the author, is concerned, the answer to both questions is in the negative. However, it is clear that cement in the ball-milled slurries of the present work must have been very close to complete hydration at the end of the experiment. The values of  $w_n^0$  reported are thus thought to be reliable estimates of chemically combined water at full hydration.

Defining the end point of the hydration process in the hardened mortars as the stage at which  $d\alpha/dt$  is effectively zero, it is clear that the portland cements having large values of  $w_0$  and the cements containing blast-furnace slag were capable of further reaction at the end of this part of the investigation. The situation in regard to these mixes will only be clarified when the results of further tests at ages of up to 10 years become available. In the meantime values of  $\alpha$  at 448 days are tentatively adopted as terminal values in the few mixes concerned since these are unlikely to be in error by more than about 10 percent. In the case of mixes from series 254-9 (1), the condition that  $d\alpha/dt$  is effectively 0 applied to the majority of results quoted in this report.

#### Constancy of $w_e/w_n w_0$ at Limiting Hydration

The conditions governing limiting hydration for the cement reported by Powers (6) may, with fair approximation, be represented by the following functions: for the zone of incomplete hydration, i. e.,  $0 < w_0 < 0.38$ ,

$$\frac{w_e}{w_n} = 1.170 \quad (10)$$

and for complete hydration, i. e.,  $0.38 < w_0 < 0.75$ ,

$$\frac{w_e}{w_n} = 4.950 w_0 - 0.667 \quad (11)$$

where  $w_n$  is determined by oven-drying.

Equations 10 and 11 are represented by the dotted lines in Figure 7, and values of  $w_e/w_n$  vs  $w_0$  calculated from other data (1, 9, 10) are plotted on the same diagram. Of these latter points, those belonging to comparable cements appear to lie on straight lines passing through the origin, with the slope of each line depending on the  $C_3A$  content of the cement. It appears that the simple straight line relationship

$$\frac{w_e}{w_n} = w_0 \text{ (constant)} \quad (12)$$

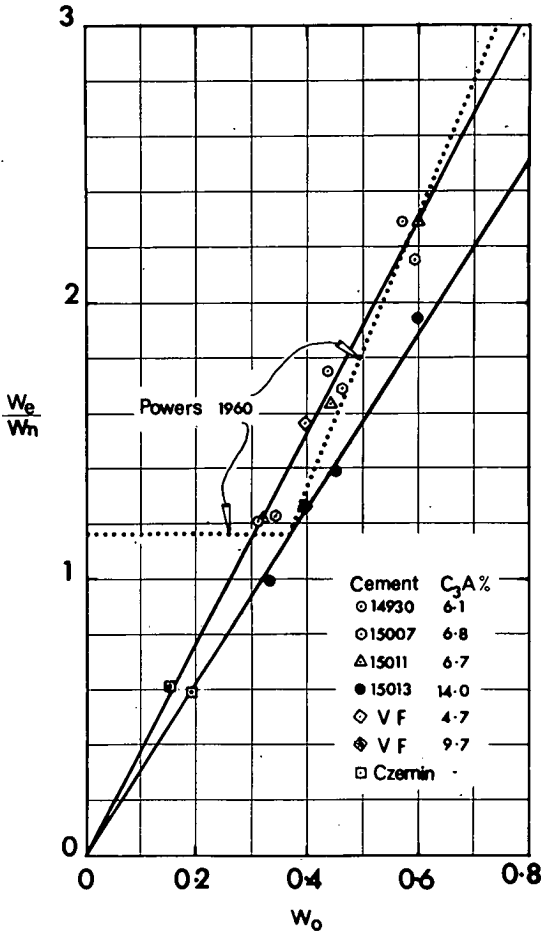


Figure 7. Relation between  $w_e/w_n$  and  $w_o$  from various sources.

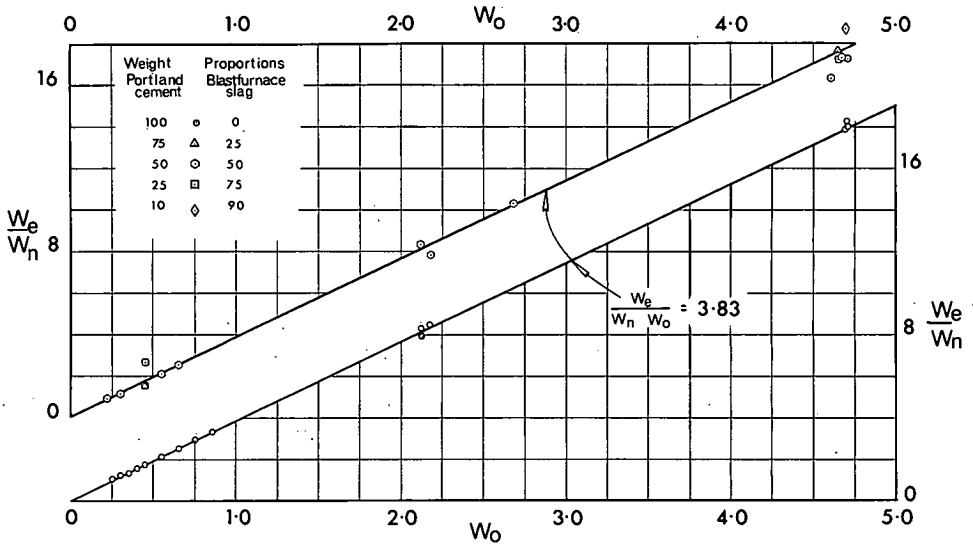


Figure 8. Relation between  $w_e/w_n$  and  $w_o$  for mixes in the present series.

might, with fair accuracy, define the conditions for cessation of hydration in all mixes having water/cement ratios above 0.25 as well as for Czernin's specimens having water/cement ratios of 0.15 and 0.19.

The relation between  $w_e/w_n$  and  $w_o$  for the present series of tests is given in Tables 3, 4 and 5 and in Figure 8. Although there is some doubt whether certain points on these curves truly represent ultimate hydration, there is little doubt that both ball-milled samples and those having low water/cement ratios had reached this stage. Since these mixes included different cements and water/cement ratios, ranging from 0.25 to about 4.7, the agreement with Eq. 12 is remarkable. The evidence appears to favor the proposition that hydration stops when the ratio  $w_e/w_n w_o$  reaches a certain critical value rather than that stoppage should be governed by discontinuous functions such as those proposed by Powers (6). The author is unfortunately unable to suggest any model for which the ratio  $w_e/w_n w_o$  takes on physical meaning.

#### Constancy of $A_c$ at Limiting Hydration

Reference to Tables 4 and 7 suggests that hydration stops when  $A_u$ , a quantity related to that part of the surface area of unhydrated cement which is in contact with water, reaches a certain finite minimum value. This conclusion, although well supported by experiment, at least in respect to the solid mortar mixes, should not be construed as a law of nature. The grossly simplified model cement upon which Eqs. 6, 8, 9 and therefore  $A_u$  are based, deviates in many important respects from the highly complex substance found in nature. The influence of such factors as particle size distribution, variation of chemical composition and therefore reaction rate with particle size, variation of porosity within the gel coatings, dependence of reaction rate on diffusion phenomena and the instability of gel structure may at the present state of knowledge be assessed qualitatively but not quantitatively. The present study is therefore confined to empirical equations based on a simple, but admittedly unreal, model.

It is of interest to note that ball-milled samples have much lower values of  $A_u$  at limiting hydration than the solid mortars. Equations 6, 8 and 9 preclude the possibility of complete hydration if  $A_u$  is indeed a finite constant which is characteristic of the cement. On the other hand if complete hydration is possible  $A_u$  must approach zero as the cement is finally consumed. In a real cement it may be assumed that  $A_u$  varies according to the particle size distribution since the finer fractions are consumed at an early age and coarser particles are probably never completely hydrated.

Validity of the proposition that hydration stops when  $A_u = \text{constant}$  should perhaps be restricted to a definite range of water/cement ratios, say from 0.25 to 0.85. In contrast to this, the alternative proposition that hydration stops when  $w_e/w_n w_o = \text{constant}$  appears to be applicable to the whole range of mixes considered.

#### Relationship Between $w_e/w_n w_o$ and $A_c$

For the series of mixes considered in the present tests it appears that the ultimate degree of hydration may be estimated from either of the following empirical equations:

$$\frac{w_e}{\alpha_u w_n w_o} = 3.83 \quad (12a)$$

or

$$A_c = 0.145 \quad (13)$$

Substitution of Eq. 2 in Eq. 12a gives an estimate of the ultimate degree of hydration  $\alpha_1$  in terms of the water/cement ratio:

$$\alpha_1 = \frac{1.031 w_o}{0.194 + w_o} \quad (14)$$

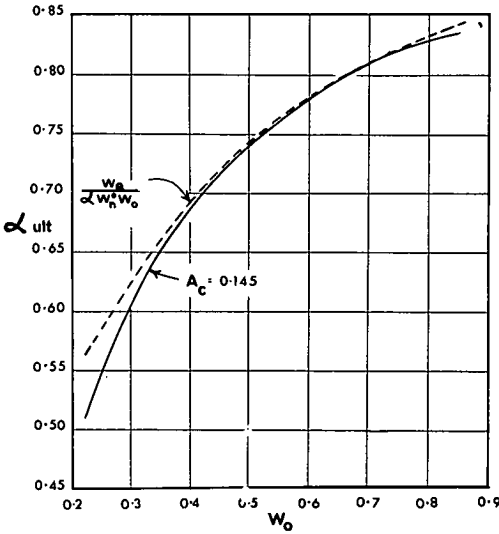


Figure 9. Ultimate value of the hydration factor according to Eqs. 14 and 15.

Equation 13 may be rewritten in the form

$$0.145 = (1 - \alpha_2)^{2/3} \left[ 1 - \left( \frac{1.602 \alpha_2}{\alpha_2 + 0.815} \right)^{2/3} \right] \tag{15}$$

where substituted values of the quantities  $w_n^0$  and  $k$  are those obtained for portland cement OP1. Graphs of the ultimate values of  $\alpha$  obtained from these equations against  $w_0$  are shown in Figure 9. It is seen that the two functions correspond closely over a wide range of water/cement ratios. It is of interest to note that in terms of Eq. 14, complete hydration is impossible in pastes having water/cement ratios below about 6.25.

In Table 8 values of  $\alpha_1$ ,  $\alpha_2$  and the ratios of  $\alpha_1$  and  $\alpha_2$  to the observed values of  $\alpha_{ult}$  under the appropriate terminal conditions are given. It is seen that Eqs. 14 and 15 both yield estimates of  $\alpha_{ult}$  which are, in the majority of cases, within a few percent of the observed values. In the case of Powers' (6) data, the "observed" values of  $\alpha_{ult}$  in Table 8 were calculated from Eqs. 10 and 11. These appear to be in poor agreement with values predicted by means of Eqs. 14 and 15. It may be noted, however, that over the range  $0.25 < w_0 < 0.85$ , values of the ratio of calculated to observed values of  $\alpha_{ult}$  do not deviate appreciably from the respective mean values. For instance, taking the six observed values calculated from Eqs. 10 and 11,  $\alpha_1/\alpha_{ult} = 0.78 \pm 0.07$  and  $\alpha_2/\alpha_{ult} = 0.79 \pm 0.05$ .

Equations 10 and 11, used to translate Powers' data to the oven-dried basis, are only approximately correct and it is hardly surprising that values based on these equations should differ from the estimated values by about 12 percent. It is suggested that values of  $\alpha_{ult}$  corresponding to Powers' discontinuous function might well be satisfactorily predicted by means of equations similar to 14 and 15 providing that  $w_n$ ,  $k w_n^0$  and  $g$  are suitably defined.

Stoppage of Hydration and the Gel-Space Ratio

The "gel" component of the gel-space ratio as calculated by Powers (6) is the bulk volume of the porous cement hydrate. In Eq. 6 C is the ratio of the absolute volume of cement hydrate to the volume of space in which it is deposited. C is therefore a measure of the gel-space ratio with the main difference that it is not necessary to make an assumption as to the respective specific volumes of free and bound water or to rely on an estimate of characteristic porosity of the gel. The gel-space ratio X is approximately equal to C multiplied by a constant, which for minimum porosity in the gel pores is equal to 1.39 (6).

TABLE 8  
COMPARISON OF  $\alpha_0$ , THE OBSERVED DEGREE OF HYDRATION ON  
MATURE PASTES, WITH  $\alpha_1$  AND  $\alpha_2$

Source	$w_0$	$\alpha_0$	$\alpha_1$	$\alpha_1/\alpha_0$	$\alpha_2$	$\alpha_2/\alpha_0$	
Powers 1960 (6)	0.25	0.669	0.549	0.83	0.550	0.83	
	0.35	0.920	0.671	0.73	0.656	0.72	
	0.45	1.000	0.715	0.71	0.716	0.72	
	0.65	1.000	0.789	0.79	0.796	0.80	
	0.75	1.000	0.806	0.81	0.816	0.82	
	0.85	1.000	0.833	0.83	0.834	0.83	
Powers 1947 (1)	0.311	0.636	0.636	1.00	0.620	0.98	
	0.344	0.696	0.660	0.95	0.647	0.93	
	0.319	0.648	0.640	0.99	0.624	0.96	
	0.443	0.705	0.720	1.02	0.711	1.01	
	0.464	0.763	0.725	0.95	0.721	0.95	
	0.442	0.739	0.715	0.97	0.711	0.96	
	0.573	0.739	0.771	1.04	0.768	1.04	
	0.595	0.817	0.779	0.96	0.777	0.95	
	0.595	0.780	0.779	1.00	0.777	1.00	
	0.332	0.768	0.650	0.85	0.638	0.83	
	0.453	0.846	0.722	0.86	0.716	0.85	
	0.599	0.888	0.791	0.89	0.779	0.88	
	Verbeck and Foster (9)	0.400	0.573	0.695	1.21	0.690	1.20
		0.400	0.671	0.695	1.04	0.690	1.03
0.400		0.662	0.695	1.05	0.690	1.04	
0.400		0.787	0.695	0.88	0.690	0.88	
0.400		0.703	0.695	0.99	0.690	0.98	
Present investigation— portland cement	0.25	0.549	0.586	1.07	0.550	1.00	
	0.30	0.608	0.626	1.03	0.611	1.00	
	0.35	0.671	0.665	0.99	0.656	0.98	
	0.40	0.692	0.695	1.00	0.690	1.00	
	0.45	0.715	0.720	1.01	0.716	1.00	
	0.55	0.758	0.763	1.01	0.763	1.01	
	0.65	0.789	0.795	1.01	0.796	1.02	
	0.75	0.806	0.819	1.01	0.816	1.01	
	0.85	0.833	0.840	1.01	0.834	1.00	
	2.13	0.972	0.945	0.97	0.945	0.97	
	2.13	0.969	0.945	0.98	0.945	0.98	
	2.13	0.927	0.945	1.02	0.945	1.02	
	4.70	0.980	0.990	1.01	0.945	0.96	
	4.68	0.998	0.990	0.99	0.945	0.95	
	4.70	0.992	0.990	1.00	0.945	0.95	
2.17	0.929	0.990	1.02	0.945	1.02		
Present investigation— 50% portland cement, 50% blast-furnace slag	0.22	0.501	0.549	1.09	0.510	1.02	
	0.30	0.617	0.626	1.01	0.611	0.99	
	0.45	0.759	0.720	0.95	0.716	0.95	
	0.55	0.752	0.763	1.01	0.763	1.01	
	0.65	0.765	0.795	1.04	0.796	1.04	
	2.18	0.940	0.949	1.02	0.945	1.01	
	2.68	0.898	0.963	1.07	0.945	1.05	
	2.12	0.897	0.946	1.05	0.945	1.00	
	4.67	0.957	0.990	1.04	0.945	0.99	
	4.71	0.992	0.990	1.00	0.945	0.95	
	4.61	0.996	0.990	0.99	0.945	0.95	
75/25	0.45	0.789	0.720	0.91	0.716	0.91	
	4.65	0.992	0.990	1.00	0.945	0.95	
25/75	0.45	0.518	0.720	1.39	0.716	1.38	
	4.65	0.984	0.990	1.01	0.945	0.97	
10/90	4.61	0.903	0.990	1.10	0.945	1.05	

Note:  $\alpha_1 = \frac{1.031 w_0}{0.194 + w_0}$  and

$$\alpha_2 \text{ derived from } A_c = (1 - \alpha_2^2)^{1/3} \left[ 1 - \left( \frac{1.604 \alpha}{\alpha + 3.22 w_0} \right)^{2/3} \right] = 0.145$$



Reference to Table 4 shows that the ratio  $C$  varies systematically with  $w_0$  but that for  $w_0$  varying from 0.25 to 0.35  $C$  lies within a range of about  $\pm 5$  percent of a mean value of  $C = 0.623$ . It thus appears that Powers' concept of limiting hydration due to constriction of space (1, 6) in the zone of low water/cement ratios is supported by the experimental data.

### Strength and the Gel-Space Ratio

Powers has proposed various empirical functions (1, 6, 11) connecting the crushing strength and either  $\alpha w_n^0/w_0$  or  $X$ . For the purpose of this report such equations may be considered to be of the forms

$$\sigma_{16} = A_0 + A_1 \frac{\alpha w_n^0}{w_0} \quad (16)$$

or

$$\sigma_{17} = f_c^0 C^n \quad (17)$$

where  $A_0$ ,  $A_1$ ,  $f_c^0$  and  $n$  are constants and the terms  $w_n^0/w_0$  and  $C$  are measures of the extent to which space initially filled with water has become replaced with material possessing structural strength.

From a study of Figure 4, it is clear that the range of validity of these equations does not include cases in which hydration has stopped, since strength continues to improve while  $\alpha$  remains constant. This may be explained in terms of a metamorphosis of the colloidal hydrate to microcrystalline material (6, 12). Intuitively it is felt that this aging process implies a strengthening of solid bonds. It is also known (7) that water in areas of restricted adsorption as found in gel pores exercises a weakening effect. Increase in the technical strength after hydration has stopped is therefore thought to depend on crystal growth on the one hand and a diminution of the effect of a weakening agency on the other. It should be noted, however, that both of these factors might conceivably lead to an increase in hydration, due first to increased exposure of unhydrated cement, and second to a change in the free energy of pore water.

### CONCLUSIONS

1. In most, if not all, cement pastes hydration stops before the cement is totally consumed. The ultimate degree of hydration  $\alpha_{ult}$  may be estimated from one of the following equations:

$$\alpha_{ult} = \frac{1.031 w_0}{0.194 + w_0} \quad (14a)$$

or

$$(1 - \alpha_{ult})^{2/3} \left[ 1 - \left( \frac{1.609 \alpha_{ult}}{\alpha_{ult} + 0.815} \right)^{2/3} \right] = 0.145 \quad (15a)$$

2. The range of validity of published relationships between strength and the gel-space ratio does not extend to mature pastes having low water/cement ratios.

### ACKNOWLEDGMENTS

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## Appendix

## NOTATION

- $w_0$  = initial water/cement ratio by weight  
 $w_t$  = total water/cement ratio by weight  
 $w_e$  = evaporable water/cement ratio by weight  
 $w_n$  = nonevaporable water/cement ratio by weight  
 $w_n^0$  = nonevaporable water/cement ratio by weight for fully hydrated cement  
 $\Delta w$  = quantity of water taken up from an external source in order to maintain saturation of paste, expressed as weight per unit weight of cement  
 $k = w_n/\Delta w$   
 $g$  = apparent density of cement, gm/cc  
 $\alpha$  = the weight ratio of hydrated cement =  $w_n/w_n^0$   
 $t$  = age of specimen after addition of mixing water  
 $d\alpha/dt$  = time rate of hydration  
 $\alpha_{ult}$  = ultimate degree of hydration  
 $\alpha_1$  = ultimate degree of hydration, computed from Eq. 14  
 $\alpha_2$  = ultimate degree of hydration, computed from Eq. 15  
 $V_{hc}$  = absolute volume of hydrated cement, cc/gm  
 $V_{uc}$  = absolute volume of unhydrated cement, cc/gm  
 $C$  = ratio of the absolute volume of the hydration products to the space available to accommodate these products  
 $A$  = surface area of unhydrated cement in a grain originally of unit diameter

$A_c$  = area of unhydrated cement exposed to water per unit of original surface in unhydrated cement

$A_u$  = portion of surface area  $A$  in contact with chemically free water

$X$  = ratio of the bulk volume of gel to the space in which it is contained

$\sigma$  = cube crushing strength, psi

$f_c^0$  = cube crushing strength when  $X = 1$

$n$  = constant

$A_0$  = constant

$A_1$  = constant