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EFFECT OF GRANULOMETRIC COMPOSITION OF CEMENT ON THE PROPERTIES OF PASTES, MORTARS, AND CONCRETES

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ABSTRACT

Data obtained in studies of five laboratory-ground clinkers and one commercial cement are presented. Each of the ground clinkers was separated into the following five nominally sized fractions: 0 to 7, 7 to 22, 22 to 35, 35 to 55, and >55 microns. The commercial cement was separated into only four fractions, no separation being made of the material coarser than 35 microns. Tests were made on the individual fractions as well as on four cements prepared by blending the fractions in various proportions. The specific surfaces of these blended cements ranged from 1,350 to 3,300 cm²/g. It was found that the 0-7 micron material is very valuable because of the plastic qualities which it confers upon the concrete mixes and also because of the high contribution which it makes to the early strength. The other four fractions were found lacking in plasticity and the ability to hold water, and the rate of strength development decreased with increasing grain size. The contribution of the 0-7 micron fraction to the strengths of the blended cements was calculated by an algebraic method based on the assumption that the contribution of any fraction to the strength of a blended cement is equal to the product of the decimal part of the blend composed of that fraction and the strength of the fraction when tested by itself. The values thus calculated were found to be of the order which might be expected. The analysis of all the strength data tended to prove that the compressive strength of concrete is very nearly a direct function of the amount of cement which has reacted with water. When the strengths were plotted against specific surface, one line was obtained for the blended cements and another line for the individual fractions. When these same strengths were plotted against quantities which should at least be approximations of the amount of hydrous material, all of them fell on one line.

CONTENTS

	Page
I. Introduction.....	420
II. Preparation and character of fractions and blended cements.....	421
1. Fractions.....	421
(a) Description of elutriation stacks.....	421
(b) Method of separating.....	422
(c) Character of fractions.....	422
(d) Chemical compositions of fractions.....	424
(e) Addition of gypsum to fractions.....	425
2. Blends of fractions.....	425
(a) Proportions and specific surfaces.....	425
(b) Method of preparation.....	426
III. Description of tests.....	426

	Page
IV. General notes on properties other than strength.....	427
1. Consistency and working qualities.....	427
(a) Fractions.....	427
(b) Blends of fractions.....	429
2. Time of setting.....	430
3. Soundness.....	431
V. Discussion of strength data.....	431
1. Introductory and general discussion.....	431
2. Theoretical considerations.....	436
3. Practical conclusions.....	446
VI. Summary.....	447

I. INTRODUCTION

The importance of knowing the relation between the particle-size distribution of cement and the properties of concrete has become more and more apparent during recent years. The study of high-early-strength cements has shown that the fineness of grinding greatly affects the rate of increase in strength. The development of plant equipment, such as finishing mills with air separators in closed circuit, making it possible to control the grinding much more closely and economically, has made the problem even more pertinent.

A considerable amount of work has already been done on the problem in other laboratories, both in this country and in Europe. An active controversy on the subject has been carried on in German technical publications during the past three or four years. Some of those who have contributed are Hans Kühl,¹ D. Steiner,² W. Weisgerber,³ Hägermann,⁴ E. Rissel,⁵ A. B. Helbig,⁶ and A. Eiger.⁷ The problem has also been studied in France and Sweden.⁸ In this country, the Portland Cement Association is at the present time carrying out an investigation of the subject at its Chicago laboratories.⁹ S. Rordam, of the Cowham System Mills, has also published results of an investigation which he carried out.¹⁰ Nevertheless, there still remains much to be done upon this problem, and the investigation described herein was undertaken with the hope of clearing up some of the controversial issues.

In this report the results obtained in studies of five different laboratory-ground clinkers and one commercially ground cement are presented. The clinkers were ground in laboratory mills without any gypsum being added. One of these clinkers (no. 5) was of the high-early-strength variety; the other four (nos. 1 to 4) were ordinary portland-cement clinkers. The commercial cement (no. 6) was a double-burned nonstaining brand of foreign manufacture.

After the clinkers had been ground to the desired degree of fineness and dried at a temperature of 110° C, they were separated into five size fractions by means of air elutriation. The nominal size ranges of the fractions were 0 to 7, 7 to 22, 22 to 35, 35 to 55, and 55 microns to the maximum size passing a no. 50 sieve. For the sake of brevity,

¹ H. Kühl, *Zement* **19**, 604, 630 (1930); *Tonind.Ztg.* **55**, 674 (1931); *Zement* **20**, 169 (1931).

² D. Steiner, *Tonind.Ztg.* **55**, 672 (1931).

³ W. Weisgerber, *Tonind.Ztg.* **55**, 933, 946 (1931).

⁴ Hägermann, *Tonind.Ztg.* **55**, 1099 (1931).

⁵ E. Rissel, *Zement* **19**, 1079 (1930).

⁶ A. B. Helbig, *Zement* **20**, 75 (1931).

⁷ A. Eiger, *Tonind.Ztg.* **56**, 532, 558 (1932).

⁸ O. Raulin, *Ciment* **35**, 342 (1930).

⁹ V. Bahrner, *Tek.Tidsk.* **59**, 114 (1929).

⁹ Report of Conservation Bureau and Research Laboratory, Portland Cement Association, Spring Meeting of 1932.

¹⁰ S. Rordam, *Rock Products*, p. 22 (July 30, 1932).

the designations 0-7, 7-22, 22-35, 35-55, and >55 will be used throughout this paper except in those cases where it may be advantageous to insert the word "micron." The foreign cement was so finely ground as delivered that it was possible to obtain only one sufficiently large fraction of material greater than 35 microns. This cement, accordingly, was separated into the four nominally sized fractions, 0-7, 7-22, 22-35, and >35 microns.

Studies were made of neat pastes, mortars, and concretes using each of the fractions individually as well as four blended cements prepared from the fractions. The fractions of the four ground portland cement clinkers and those of the commercial cement were tested without the addition of gypsum and also after 3.6 percent of gypsum had been added. Those of the high-early-strength clinker could not be tested without gypsum because of the quick initial set. It was found that 3.6 percent of gypsum was sufficient to retard the set of all but the 0-7 fraction of this clinker; the 0-7 fraction required 10 percent. The blends of the four portland-cement clinkers were tested, like the fractions, with and also without the addition of 3.6 percent of gypsum. Those of the high-early-strength clinker and the commercial cement were tested only after gypsum had been added, 3.6 percent in all cases except that of the finest blend of the clinker, to which 6.5 percent had to be added.

Throughout the remainder of this report the laboratory-ground clinkers will be referred to as cements, except when the context makes the use of the word "clinker" more desirable.

II. PREPARATION AND CHARACTER OF FRACTIONS AND BLENDED CEMENTS

1. FRACTIONS

(a) DESCRIPTION OF ELUTRIATION STACKS

The fractions were prepared in three air-elutriation stacks. The separations at 7 and 22 microns were made in the two stacks shown in figure 1. These two stacks operate in parallel, one blower supplying the air, which first enters the bottoms of the stacks, then passes upwards to the lead-off pipes connected to the dust collectors where it is forced through canton-flannel filtering bags before returning again to the blower. In the return lines, between the dust collectors and the blower, there are changeable orifices by means of which, together with differential pressure gages, the volume of circulating air, and hence the velocity of the air in the stacks, is controlled. A portion of the air from the blower is constantly by-passed through a refrigeration unit where it is cooled down to about 23° F. Upon returning to the blower the temperature of this air is raised to about 90° F. This process reduces the relative humidity to about 10 percent. Since the whole system is closed and there is no opportunity for the air to escape, the humidity of the circulating air is always kept very low. The stack in which the 35- and 55-micron separations were made is not shown in the figure, but it is of essentially the same design. The two stacks shown in the figure are 22 inches in diameter and have 6-foot straight sections with 4-foot cones. The third stack is 11 inches in diameter and has a 7-foot straight section with a 2-foot cone.

(b) METHOD OF SEPARATING

In making the separations the material was first blown in the two large stacks until most of the particles less than 7 microns in diameter had been removed. The next step consisted in blowing the residue, which was nearly all greater than 7 microns, in the same stacks at such a velocity as to effect a separation of a 7-22 fraction, which was caught in the filter bags. The residue was then blown in the 11-inch stack so as to yield a 22-35 fraction, which in turn was collected in the filter bag. After removal of the 22-35 fraction, the 35-55 fraction was blown off and collected. The residue from the last separation was sieved on a no. 50 screen, the material passing being designated as the >55 fraction. Each of the fractions was separately put through the stacks again and rebrown at the lower size limit until shown by microscopic examination to be free from undersized material. It was found necessary to do this because the fractions as caught in the filter bags always contained a considerable amount of undersized material, caused by abrasion of the particles in the lower part of the cones. By this rebrown process a clean fraction was always obtainable as a residue from the lower outlets of the cones.

(c) CHARACTER OF FRACTIONS

Photomicrographs of typical fractions are shown in figures 2 and 3. Size-distribution curves for the fractions of three of the cements were obtained by means of microscopical measurements and counts. The fractions were mounted on microscope slides in an oil having a refractive index of 1.55.¹¹ The particle images were projected on a screen and measured with a calibrated rule. All the particles in a definitely bounded area in the middle portion of the field were measured and counted. In making the measurements an attempt was made to arrive at the average visible diameter of each particle; the "diameter" taken for an elongated particle was the mean of the longest and shortest visible dimensions. Different magnifications were used for different sized fractions; the finest fraction was magnified 5,700 times and the largest sized fraction 625 times. The weight-size distribution curves for the fractions of cement no. 4 are presented in figure 4. Those for the other two cements were quite similar. The size designations 0-7, 7-22, 22-35, 35-55, and >55 microns were arbitrarily chosen. It is seen in the figure that any two successive fractions overlap considerably.

The total surface area contained in unit weight of material, or what is commonly called the "specific surface", was calculated for each of the fractions from the data used in plotting the distribution curves. The relation between specific surface and distribution is given by the equation

$$ss = \frac{\sum nd^2}{\sum nd^3} 19050,$$

where ss is the specific surface in cm^2 per gram, n is the number of particles of diameter d microns, and 19050 is the surface in cm^2 of one gram of particles of diameter 1 micron and density of 3.15. The

¹¹ For a discussion of the effect of the refractive index of mounting medium, see *A sedimentation method for the determination of the particle size of finely divided materials (such as hydrated lime)*, by Dana L. Bishop, BS J. Research 12, 173 (1934) RP642.

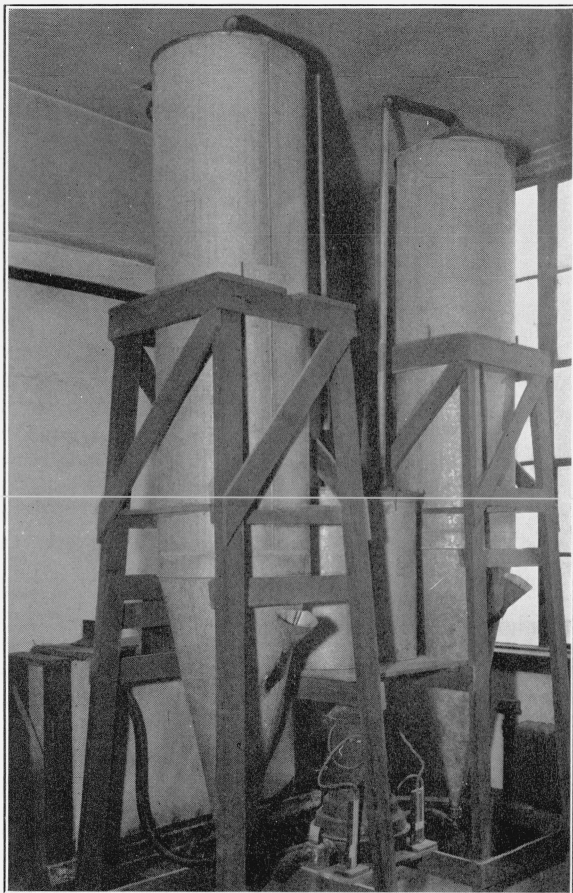


FIGURE 1.—*Air elutriation stacks.*

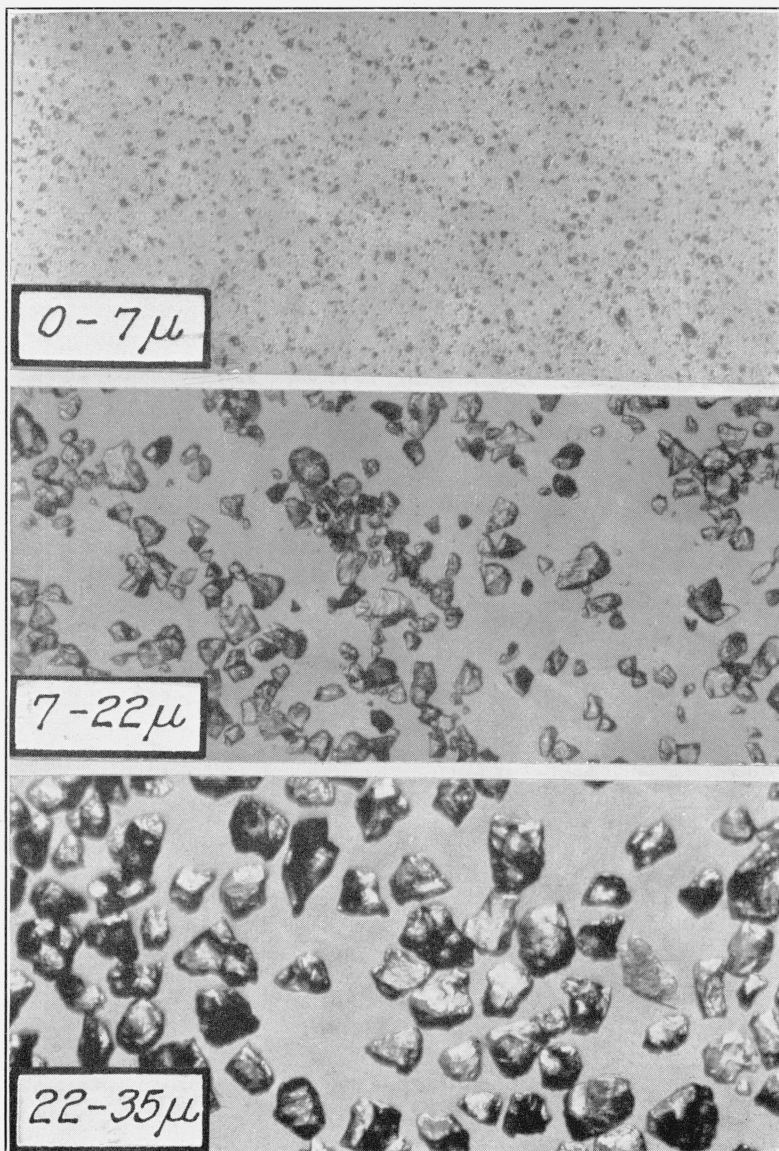


FIGURE 2.—Photomicrographs of the 0-7, 7-22, and 22-35 fractions.
(Magnification $\times 260$.)

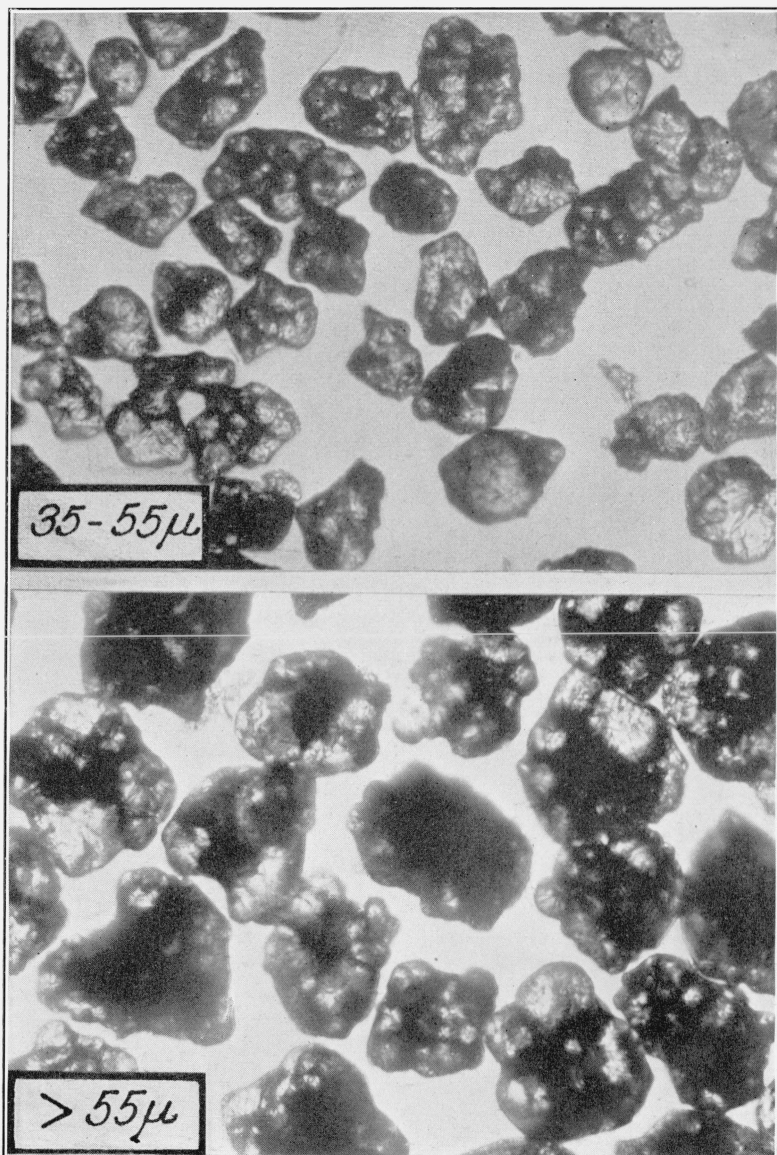


FIGURE 3.—Photomicrographs of the 35-55 and >55 fractions.
(Magnification $\times 260$).

specific surfaces obtained by this method for the fractions of cements 1, 3, and 4 are given in table 1 (A). Each of the values given is the average of the values obtained by calculation from measurements of 100 or more particles from each of two slides.

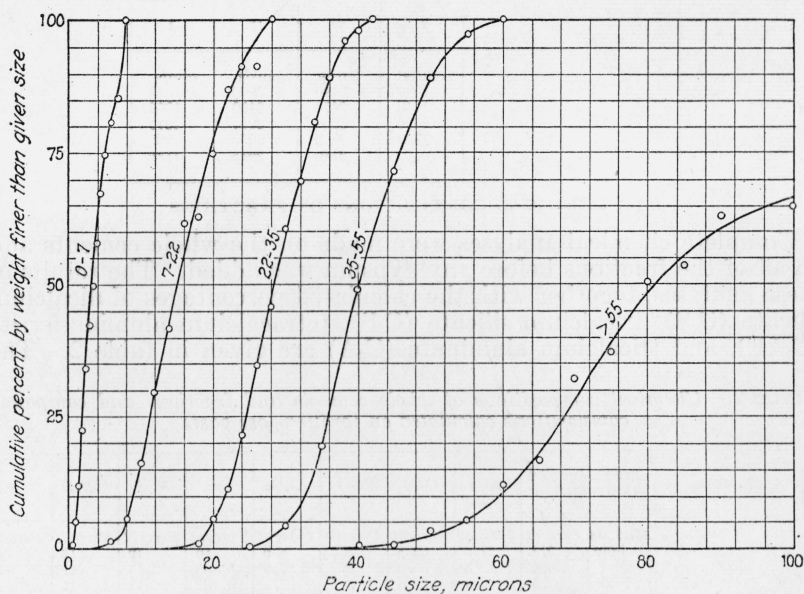


FIGURE 4.—Size distribution of fractions.

TABLE 1.—Specific surface data

(A) Specific surface of fractions as determined from microscopical counts:

Cement no.	Specific surfaces of fractions				
	0-7 μ	7-22 μ	22-35 μ	35-55 μ	>55 μ
1	cm ² /g 6600	cm ² /g 1470	cm ² /g 800	cm ² /g 440	cm ² /g 240
3	5000	1280	640	380	170
4	6380	1300	680	440	225
Average	6000	1350	710	420	210

(B) Proportion of each fraction in blends and specific surfaces of blended cements:

Blend	Percentage by weight, of fractions					Specific surface ¹
	0-7 μ	7-22 μ	22-35 μ	35-55 μ	>55 μ	
F	20	20	20	20	20	cm ² /g 1750
G	30	32	25	10	3	2450
H	47	24	20	7	2	3300
I	12	23	20	13	32	1300

¹ Calculated from average microscopical values for fractions of cements 1, 3, and 4.

TABLE 1.—*Specific surface data*—Continued

(C) Specific surfaces as determined by Wagner turbidimeter:

Cement no.	Specific surface of blend			
	F	G	H	I
	cm ² /g	cm ² /g	cm ² /g	cm ² /g
1.....	1690	2490	2960	1240
2.....	1740	2470	3190	1360
3.....	1620	2250	2950	1270
4.....	1720	2610	3050	1280
5.....	2240	2945	1130

(d) CHEMICAL COMPOSITIONS OF FRACTIONS

Complete chemical analyses were made on the whole cements and on all of the fractions before any gypsum was added. The results of these analyses, together with the calculated percentages of dicalcium silicate (C₂S), tricalcium silicate (C₃S), tetracalcium aluminoferrite (C₄AF), and tricalcium aluminate (C₃A) are given in table 2. The

TABLE 2.—*Chemical compositions of whole cements and fractions and compound compositions calculated on ignition-loss basis*

Cement no.	Frac-tion	Loss on ignition	SiO ₂	CaO	Fe ₂ O ₃	Al ₂ O ₃	C ₃ S	C ₂ S	C ₄ AF	C ₃ A
			Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
1.....	Whole	2.4	21.0	65.5	3.7	6.9	56	19	11	12
	0-7	6.4	20.3	65.3	3.6	7.3	59	14	11	13
	7-22	2.5	20.4	65.8	3.5	7.1	62	11	11	13
	22-35	1.5	21.2	65.5	3.6	7.2	52	22	11	13
	35-55	1.1	21.1	64.8	3.7	7.4	49	24	11	13
	>55	0.9	21.1	64.4	3.7	7.5	47	25	11	14
2.....	Whole	1.3	22.0	66.2	2.5	6.6	54	23	8	13
	0-7	2.8	22.0	66.2	2.1	6.4	57	20	6	13
	7-22	1.2	22.3	66.5	2.2	6.5	54	23	7	14
	22-35	0.7	22.2	66.0	2.6	6.0	56	22	8	12
	35-55	0.6	21.6	65.6	3.0	6.7	54	22	9	13
	>55	0.7	21.2	65.2	3.5	6.9	53	22	11	12
3.....	Whole	1.4	21.0	65.5	2.3	7.1	56	18	7	15
	0-7	4.1	20.7	65.6	2.3	6.7	62	13	7	14
	7-22	1.5	21.0	66.0	2.2	6.3	64	12	7	13
	22-35	0.8	21.6	65.5	2.3	6.6	56	20	7	14
	35-55	0.6	21.6	65.1	2.4	7.1	49	25	7	15
	>55	0.5	21.9	64.5	2.5	7.0	46	28	8	14
4.....	Whole	0.7	23.8	65.4	5.6	3.5	55	27	17	1
	0-7	2.6	21.0	65.7	7.1	4.2	64	13	20	1
	7-22	0.8	23.0	66.3	5.4	3.5	64	18	16	0
	22-35	0.5	24.7	65.6	5.0	3.4	51	33	15	1
	35-55	0.4	24.8	65.2	5.4	3.3	46	37	16	0
	>55	0.3	25.0	65.4	5.8	3.7	43	39	18	0
5.....	Whole	1.2	19.6	66.4	2.5	6.9	72	2	8	14
	0-7	2.2	19.3	65.9	2.5	6.8	72	1	8	14
	7-22	0.7	20.4	66.7	2.4	6.7	67	8	7	14
	22-35	0.7	20.1	66.9	2.4	6.8	70	5	7	14
	35-55	0.6	19.4	66.8	2.5	7.3	72	1	8	15
	>55	0.3	19.5	66.5	2.6	7.4	70	3	8	15
6 ^a	Whole	4.8	21.1	69.4	0.5	1.7	63	14	1	4
	0-7	9.5	16.3	70.0	0.4	1.0	49	10	1	2
	7-22	5.2	20.3	70.7	0.5	1.0	76	1	1	2
	22-35	2.2	23.8	70.1	0.6	1.3	76	11	2	2
	>35	1.5	25.5	66.8	0.6	2.0	51	35	2	4

^a 2CaO. Fe₂O₃.

^b It is quite probable that cement no. 6 was partially hydrated and there is therefore some doubt as to its compound composition. The amounts of "free lime" present were determined by the ammonium-acetate method, which yields both Ca(OH)₂ and CaO, and were found for the whole cement and the fractions as given above to be as follows: 11, 24, 12, 4, and 1. In calculating the compound compositions given in the table the free lime was assumed to be all CaO although it possibly consisted largely of Ca(OH)₂. Since there is no way of knowing the exact source of the so-called free lime in a partially hydrated cement, the compound composition cannot be calculated with certainty. If the C₃S and C₂S in the "whole" fraction are calculated for the condition before the partial hydration (i. e., assuming no uncombined CaO) it is found that there were present of 80.0 percent of C₃S, 0.0 of C₂S, and 7 of uncombined CaO.

data on the five ground clinkers have been previously discussed in a paper entitled *Chemical analyses of the particles of various sizes of ground cement*, by E. T. Carlson and P. H. Bates,¹² published in the Oct. 22, 1932 issue of *Rock Products*.

As was brought out in this previous paper, the data show that there is a considerable amount of variation between the different fractions of any one cement as to chemical composition and potential compound composition. The finer fractions are in all cases higher in ignition loss than the coarser ones. The tricalcium silicate shows a tendency to be more concentrated in the finer, and the dicalcium silicate in the coarser fractions. The tricalcium aluminate and the tetracalcium aluminoferrite seem to be about equally distributed between the fine and coarse particles.

The nonstaining cement, no. 6, which had not been analyzed at the time that the first paper was published, differs from the others in that it contains a very high percentage of "free" lime. The fact that most of this so-called "free" lime is found in the 0-7 fraction tends to indicate that this lime actually occurred largely in the hydrated form.¹³ In other respects the cement exhibits the same general tendencies as the clinkers. When allowance is made in the case of the 0-7 fraction for the large portion of the lime which was not contained in the four usual constituents, the difference in tricalcium silicate between this fraction and the next two is very considerably reduced.

(e) ADDITION OF GYPSUM TO FRACTIONS

In adding the gypsum to the 0-7 fraction, the total required amount was first mixed with one kilogram of cement for one-half hour in a small mill containing a charge of stone pebbles. This mixture was then transferred to a larger mill, the remainder of the cement and a few wooden balls were added, and the mill was rotated for one-half hour. In the cases of the other four fractions the required amount of gypsum was added directly to the total amount of cement and the whole mixed with wooden balls for one-half hour. The gypsum used in this investigation was ground so as to be about 50 percent finer than 4 microns and 90 percent finer than 8 microns.

2. BLENDS OF FRACTIONS

(a) PROPORTIONS AND SPECIFIC SURFACES

The proportions of the fractions and the specific surface data for the blended cements prepared from the fractions, for cements 1 to 5 inclusive, are presented in table 1 (B) and (C). The specific surfaces were determined by direct calculation from the microscopical values for the fractions and also by means of the Wagner turbidimeter.¹⁴ The weight and surface distributions are shown graphically in figure 5.

In preparing the four blends of cement no. 6, a total percentage of >35-micron material, which was equal to the sum of the percentages of the two largest sized fractions in the corresponding blends of the other cements, was used. Since this >35-micron material of cement no. 6 consisted mostly of material finer than 55 microns, its substitution for the >55 fraction as contained in the blends of the other

¹² The data are the same except that in the previous paper the constituents were presented as calculated on the no ignition-loss basis. In order to more accurately define the actual sizes, the nominal sizes 22-35, 35-55, and >55 have been adopted instead of 22-45, 45-75, and >75, respectively, for the largest sized fractions.

¹³ Each of the nine hydrated limes studied by Bishop contained at least 60 percent of material finer than 10 microns. Quicklimes are very seldom ground to such a high degree of fineness. See footnote 11, p. 422.

¹⁴ Proc. Am. Soc. Testing Materials **33**, II, 553 (1933).

cements probably had the effect of making the specific surfaces of the no. 6 blends slightly greater than those of the other 5 cements. No specific surface determinations were made on the blends of cement no. 6.

(b) METHOD OF PREPARATION

The blends without gypsum were prepared by placing together the properly weighed fractions in a laboratory mill and mixing with wooden balls for a half hour. The same general procedure was used in adding the gypsum to the blends as was used in adding it to the 0-7 fraction. The gypsum was first mixed for one-half hour with one kilogram of 0-7 material in a small mill with a small charge of stone pebbles. This mixture was then transferred to a larger mill; the remainder of the 0-7 and the proper weights of the other fractions were added, and the whole was mixed with the aid of a few wooden balls for one-half hour.

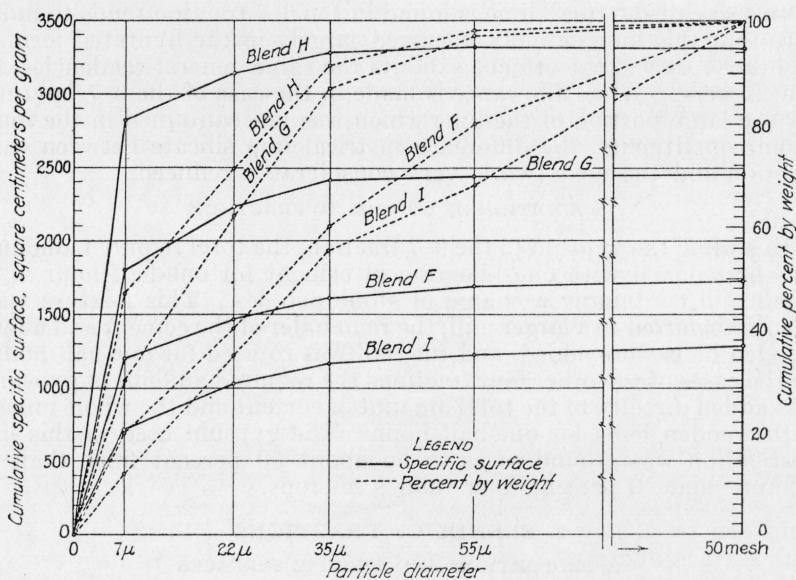


FIGURE 5.—Specific surface and weight distributions of blends.

III. DESCRIPTION OF TESTS

Each of the fractions and the four blends prepared from the fractions were tested for consistency, time of set, soundness, tensile and compressive strength. Strength tests were made on 1:3 mortar briquettes and 3- by 6-in. concrete cylinders at 1, 3, 7, and 28 days and 1 year. Three specimens were tested at each age.

The procedures of Federal Specification for Portland Cement, SS-C-191, were followed as closely as possible in making the tests of the neat pastes and the 1:3 mortars. However, only one attempt was made to arrive at a normal consistency, since it was realized that this test could have very little meaning, especially in the case of the individual fractions. Water was added until the operator judged the paste to be of about normal consistency; the Vicat reading was then taken and the pat made irrespective of the reading. The time of

setting was observed by means of Gillmore needles, for the first seven hours, beyond which the time of set was not determined.

In making the mortar specimens an amount of water equal to 15.0 percent by weight of the dry cement was used throughout on the 0-7 micron material. For the other fractions and the four blends this percentage was maintained at 11.0. In the case of some of the coarser fractions it was found necessary to seal the bottoms of the molds with an asphaltic material in order to keep the water from seeping out.

The mix from which the concrete cylinders were made was proportioned 1:2 $\frac{1}{4}$:3 $\frac{3}{4}$ (cement:sand:coarse aggregate) by dry rodded volumes. Potomac River sand with a fineness modulus of 2.84 was used. The coarse aggregate consisted of one part no. 4 to $-\frac{3}{8}$ in. and one part $\frac{3}{8}$ in. to $\frac{1}{4}$ in. gravel, the fineness modulus being 6.50. The fineness modulus for the combined sand and gravel was 5.1. The cement was assumed to weigh 94 lb./ft.³, although actually there were considerable variations in bulk density between the different fractions and blends. A cement-water ratio, by weight, equal to 1.25 was used throughout on the 0-7 micron material. For the other four fractions and the blends this ratio was maintained at 1.80. Enough water was added to compensate for absorption by both coarse and fine aggregate. The concrete was tamped 25 times in each of three layers as it was placed in 3- by 6-in. tin cans. When the cans had been filled, covers were put on and sealed with asphalt in order to prevent loss of water by evaporation. These cans were then stored at $70 \pm 3^\circ$ F until the time of test, when the cylinders were removed from the cans and capped with plaster of paris.

IV. GENERAL NOTES ON PROPERTIES OTHER THAN STRENGTH

1. CONSISTENCY AND WORKING QUALITIES

(a) FRACTIONS

As was to be expected, the individual fractions were found to vary greatly in properties such as ability to hold water, plasticity, and ease of molding and troweling. The extent of some of these variations can be observed in table 3. The 0-7 fraction, having a very high surface, fell in a class by itself; the other four fractions ranged rather uniformly from the 7-22 fraction, which was not vastly different from an ordinary portland cement, to the >55 fraction which behaved very much like a fine sand.

The 0-7 fraction required a very high percentage of water for neat pastes of approximately normal consistency, and it was found necessary to use very low cement-water ratios in order to obtain workable mortars and concretes. The resulting pastes, mortars, and concretes were in all cases very plastic. They were also characterized by an extreme stickiness, which made the neat pastes and mortars difficult to trowel. There were in no cases any signs of water segregation from this material.

In rather marked contrast to this behavior of the 0-7 micron material, the four coarser fractions were all more or less deficient in the power to hold water and also in plasticity and good working qualities. When the neat paste made from the 7-22 fraction was put in the Vicat ring a very thin paste would usually come to the top and some would seep out under the bottom of the ring. A

similar effect was noticed in the mortars and concretes. This fraction also appeared somewhat harsh and was slightly harder to mix than a whole cement.

TABLE 3.—*Neat-paste data*

Fraction or blend	Cement no.	No gypsum						3.6 percent of gypsum					
		Penetration of needle		Time of set		Soundness	Penetration of needle		Time of set		Soundness		
		H ₂ O		Initial	Final		H ₂ O		Initial	Final			
A ¹	B ²	Hour	Hour	Per-cent	mm	mm	Hour	Hour	Per-cent	mm	mm	Hour	Hour
0-7μ	1	50.0	40	30	4.5	8	Cracked ³	47.8	13	10	4.5	7.5	Cracked. ³
	2	50.0	6	4	3.5	7-23	Cracked ³	42.0	10	14	1	5	OK.
	3	45.4	7	1	2.5	7	OK	44.0	40	38	4	8	OK.
	4	40.0	5	3	1	8	Cracked ³	43.4	40	15	1	8	Cracked. ³
	4.5							54.0	12	10	1.5	5	OK.
	6	47.0	13	5	4	7	OK	47.0	4	2	4.5	7	OK.
7-22μ	1	38.4	35	15	8	7-23	OK	36.0	32	40	8	8-23	OK.
	2	35.0	11	14	6	7-23	Cracked ³	33.0	35	40	5	7-24	OK.
	3	38.0	40	40	8	8-23	OK	36.0	38	40	7	7-24	OK.
	4	36.0	38	30	7-24	36	OK	31.8	32	40	7	7-23	OK.
	5							33.0	24	30	6	7-23	OK.
	6	43.0	12	30	4.5	7.5	OK	43.0	13	10	5	8	OK.
22-35μ	1	32.0	27	10	7-23	28	OK	30.0	22	40	8.5	23	OK.
	2	31.0	10	9	7-23	23	OK	28.0	20	28	7	8-24	OK.
	3	30.0	10	20	1	7-24	OK	28.0	7	15	7	7-23	OK.
	4	28.4	12	20	7-24	30-48	OK	28.0	22	40	7	7-24	OK.
	5							28.0	8	15	6.5	7-23	OK.
	6	47.6	5	7	6.5	7-24	OK	48.0	13	30	6.5	7-23	OK.
35-55μ	1	30.0	3	4	5	23.5	OK	30.0	22	38	7-24	24	OK.
	2	30.0	7	1	8-24	8-24	OK	27.0	12	22	7-23	7-23	OK.
	3	30.0	11	22	7	7-24	OK	29.0	20	35	8	24-48	OK.
	4	28.0	8	15	7-24	48	OK	28.0	30	40	6-22	22	OK.
	5							28.0	17	35	7-23	7-23	OK.
	6	50.0	2	3	4	23	OK	50.0	16	35	5	23	OK.
>35μ	1	30.0	7	5	5	27	OK	28.0	20	10	7-24	28	OK.
	2	30.0	3	1	8-24	8-24	OK	28.0	25	35	7-23	7-23	OK.
	3	30.0	9	23	7	30-48	OK	29.0	28	35	7-22	30-48	OK.
	4	28.0	3	3	7-24	72	OK	30.0	35	40	6-22	22	OK.
	5							28.0	30	15	6-22	22.5	Warped.
	6												
F	1	24.0	30	10	4	23	OK	23.0	9	11	4	7	OK.
	2	23.0	3	1	3	8	OK	23.0	12	25	4	8	OK.
	3	24.0	35	37	.5	6	OK	22.0	11	15	4.5	7-22	OK.
	4	23.0	40	40	2.5	7-23	Cracked ³	22.0	40	40	4	7-24	OK.
	5							23.0	7	9	4	6.5	OK.
	6							32.4	5	2	4.5	7.5	OK.
G	1	27.6	8	13	2.5	7.5	OK	28.0	10	15	4.5	8	OK.
	2	29.6	7	2	3	8	Cracked ³	28.0	35	30	3	7	Cracked. ³
	3	26.0	9	3	.5	6	OK	25.0	8	27	4	8	OK.
	4	24.0	6	3	1.5	7-23	Cracked ³	24.0	7	10	2.5	7-24	OK.
	5							29.0	9	9	3	5	OK.
	6							35.6	8	3	4.5	7	OK.
H	1	31.4	8	7	2.5	7	OK	32.0	8	7	4	8	OK.
	2	33.0	7	2	3	8	Cracked ³	29.2	15	15	2	7	OK.
	3	30.0	13	15	.5	6	OK	29.0	12	30	4.5	9	OK.
	4	27.0	10	3	1	22	Cracked ³	27.0	10	9	1	8	OK.
	5							33.0	6	6	1	2.5	OK.
	6							36.0	6	3	4	7	OK.
I	1	22.0	11	35	5	7-23	OK	22.0	13	13	6.5	9	OK.
	2	23.0	5	2	3	8	OK	22.6	30	32	5	9	OK.
	3	24.0	35	40	1	7-24	OK	22.0	20	38	7	7-24	OK.
	4	21.0	15	5	3	7-22	Cracked ³	20.0	22	15	5	6-24	OK.
	5							22.0	6	10	5	7.5	OK.
	6							33.0	8	5	5	8	OK.

¹ Standard Vicat needle.

² 100 g needle of 5-mm diameter.

³ Pats developed cracks before attaining final set; no further distortion during steaming.

⁴ 6.5-percent of gypsum added to fraction.

These tendencies were very much accentuated in the case of the 22-35 and the 35-55 fractions. The neat pastes made from these fractions would appear quite dry, but when they were put in the Vicat ring practically clear water would rise to the surface and some would run out between the ring and glass plate. Likewise, there would always be a considerable amount of water segregation from the mortars and concretes. As to working qualities, these fractions were always definitely lacking in plasticity, and the pastes, mortars, and concretes were very harsh.

The >55 fraction differed from the 22-35 and 35-55 fractions in that the mortars and concretes made therefrom always appeared much drier and showed much less segregation than those made from the other two fractions. There was not as great a difference in this respect between the neat pastes of these three fractions as there was between the mortars and concretes, there being always a considerable amount of water segregation from the >55 neat pastes. This largest sized fraction was, of course, entirely lacking in plasticity, and it behaved under all conditions very much like a fine sand.

The addition of gypsum to the clinker fractions in some cases made the pastes noticeably smoother, and in a few instances it served to remove a tendency of the pastes to stiffen shortly after the mixing was completed. The 0-7 micron material without gypsum usually showed this tendency to stiffen immediately after mixing, but after the gypsum had been added it no longer did this. This was also true for the four coarser fractions of cements 2 and 3. It can be seen from the neat-paste data of table 3 that the Vicat penetrations are generally greater for the material containing gypsum, although on the average a lower percentage of mixing water was used. The presence of the gypsum had no noticeable effect on the amount of water segregation, except that this segregation was increased in those cases where the plain material had tended to stiffen.

(b) BLENDS OF FRACTIONS

There were also naturally rather wide variations in the working qualities of the blended cements. The two low surface blends, I and F, were quite similar to ordinary portland cements, while the two high surface blends, G and H, resembled high-early-strength cements in their behavior. Blend I was somewhat more harsh than the usual portland cement, and blend H was more plastic and also more sticky than the usual high-early-strength cement. Since medium cement-water ratios were chosen and used for all four of the blends, the I mortars and concretes were rather wet and those of the H blends were somewhat dry. There was a slight amount of water segregation from the blend I concrete mixes of cements 2 and 4 containing gypsum. The concrete mixes of the H blend were in several instances too dry to allow good fabrication of test specimens.

The percentage of water necessary for neat pastes of approximately normal consistency was found to be very nearly directly proportional to specific surface. In figure 6, the average of the percentages used for cements 1 to 4, inclusive, is shown plotted against specific surface. It is seen that a linear relationship exists. This figure also shows that the addition of gypsum made it possible to use a slightly lower percentage of mixing water.

2. TIME OF SETTING

It is possible that the data on setting time for the individual cements do not have very much quantitative significance because of the large number of variables which entered into the determinations. Neither the amount of water used nor the consistency were kept constant; only one attempt was made in each instance to arrive at a normal consistency, and as the data show, a large percentage of the pastes varied considerably from normal consistency. Another disturbing factor in the case of the fractions was the nonuniformity in the test specimens brought about by water segregation. However, when averages are considered, the data do indicate certain general trends.

The setting times seem to be closely related to specific surface; the greater the surface, the shorter the time of set. In figure 6 the

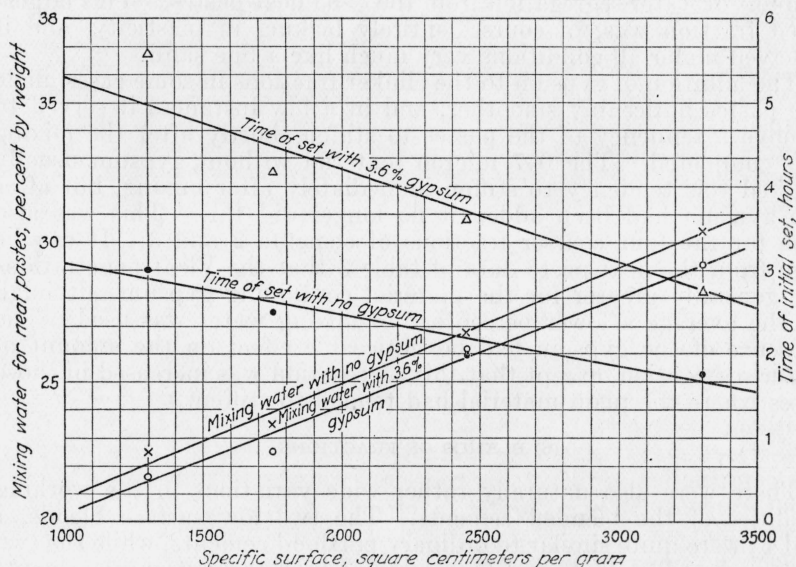


FIGURE 6.—Averages of mixing water and of times of initial set for blends as a function of specific surface.

average time of initial set of the blends for cements 1 to 4 is plotted against specific surface. It is seen that the addition of gypsum prolonged the time of initial set. The setting times of the individual fractions were not plotted because they were not determined accurately for the coarser material, but the data show that the time tends to increase as the grain size increases.

The blends of cement no. 3 without gypsum behaved in a rather unexpected manner, especially in view of the results obtained on the individual fractions. Although none of the fractions were quick setting, the four blends all had the initial set within one hour. The lower percentage of water used on the blends may have had something to do with this apparent speeding up of the setting process.

3. SOUNDNESS

If soundness is defined as the ability of a neat-paste pat to withstand 5 hours of steaming without any distortion, there is only one case of unsoundness to report. The pat made from the >55-micron material of the high-early-strength clinker no. 5 (with gypsum added) showed no signs of distortion when placed in the steam chest, but after having been steamed for 5 hours it was warped and beginning to spall. With this one exception, all of the pats survived the steam test without any noticeable ill effects.

There were, however, several instances where the pats developed shrinkage cracks in the damp-storage closet before the final set had been attained, but showed no further distortion in the steam test. Most of these cases of early shrinkage occurred in the materials to which gypsum had not been added, ten out of the thirteen cases in all being found in the "no gypsum" column of table 3. Of the individual fractions, the 0-7 was the one which most frequently developed the shrinkage cracks, and it seems probable that this shrinkage of the fine material was responsible for the similar behavior of the blends in several instances. For example, in the case of cement no. 4 without gypsum, the pats made from the blends developed a considerable number of shrinkage cracks as did the 0-7, although those made from the four other fractions had all remained intact. The same effect was noticed in cement no. 2.

V. DISCUSSION OF STRENGTH DATA

1. INTRODUCTORY AND GENERAL DISCUSSION

In examining the strength data (table 4) there are several factors which should be kept in mind. In the first place, the strengths of the fractions of any one cement should not be compared to each other without considering the variations in their chemical composition. The fractions of cements nos. 2 and 5 are probably sufficiently uniform in composition to allow direct comparisons of strength. The other four cements, however, show variations of 15 percent or more in tricalcium silicate, with corresponding differences in dicalcium silicate. Since the former compound contributes mostly to the early strength and the latter to that at the later ages, these variations would account for a part of the differences between the strengths of the fine and coarse fractions, the whole of which might at first sight be attributed to differences in surface. This positive influence of the silicate distributions is partially vitiated by the higher percentage of hydrated material in the fine fractions as indicated by the ignition loss.

Other factors which ought to be considered in studying the strength data are the differences, shown by the concrete mixes and mortars, in compactability and water retaining capacity. With the exception of the 0-7 fraction the same cement-water ratio was used throughout, and since the size gradations of the fractions and blends varied over a broad range there were naturally wide variations in their working qualities. The gradation of any one fraction or blend, however, was the same for all cements and differences in working qualities resulting from size gradation should be exhibited in like degree by the same fraction or blend of each cement.

TABLE 4.—*Strength data*
 NG=No gypsum added to the fraction or blend.
 G=3.6 percent of gypsum added.

Fraction or blend	Cement	Cement-water ratio by weight for concrete	Tensile strength in lb per sq in. 1:3 standard sand mortar ²										Compressive strength in lb per sq in. (3- by 6-in. concrete cylinders)												
			1 day		3 days		7 days		28 days		1 year		1 day		3 days		7 days		28 days		1 year		Flow		
			NG	G	NG	G	NG	G	NG	G	NG	G	NG	G	NG	G	NG	G	NG	G	NG	G	NG	G	
0-7 μ	1	1.25	215	225	365	375	410	360	415	440	320	370	620	575	1510	1480	1800	1720	2090	1900	2150	2310	33	47	
	1	1.80												1050		2070		2360		2460		3060			
	2	1.55																2160		2350				16	
	2	1.25	285	230	370	305	405	330	415	365	340	300	800	530	2020	1770	2200	2110	2890	2340	2720	2220	4	45	
	2	1.65												1530		2770		2960		3320		3410		10	
	2	1.55												1510		2960		3160		3520		3320		9	
	3	1.40														2240		2790		3170		3110		10	
	3	1.25	225	240	360	330	395	400	410	470	310	325	390	500	1700	1440	1930	1780	2355	2210	2300	2270	37	64	
	3	1.55														2270		2850		3060		3050		23	
	3	1.80																2190		2520				24	
	4	1.25	85	40	295	300	300	305	355	365	275	295	170	30	1270	1190	1530	1640	2130	2250	2350	2300	22	45	
	15	1.25														1550		1700		1930		2020		10	
	15	1.55														790		1080		1250		1610			
	25	1.25																1720		1910		1930		2100	
	6	1.25	205	200	255	200	285	250	330	275	255	210	630	550	930	790	1040	1010	1260	1200	1560	1530	42	32	
7-22 μ	1	1.80		70	120	245	195	355	405	485	415	430	90	245	735	1440	1510	2510	2810	3630	3400	4200	33	43	
	1	1.80	70	110	225	335	315	415	475	530	430	520	75	455	1260	1630	2280	2570	3760	3470	3740	3860	16	41	
	3	1.80	40	60	140	240	215	335	385	520	415	485	65	215	785	1210	1660	2190	2860	3380	2790	4000	41	33	
	3	1.25												60		500		1070		1760		2690			
	4	1.80		85	145	275	325	385	410	425	445	485	80	260	390	1370	2150	2140	2760	2840	3740	4050	45	36	
	4	1.25												80		505		770		1110		1920			
	5	1.80		145		295		460		480		405		590		2330		3640		4250		4110		12	
	15	1.55												325		1370		2320		2740		3350		40	
	25	1.25												210		820		1600		1870		1950			
	6	1.80	175	205	240	310	255	375	330	400	240	300	790	870	1620	2110	2120	2700	2550	3380	2680	3950	23	17	
	22-35 μ	1	1.80		30	40	65	85	160	170	360	400	425	30	55	270	530	710	1120	1680	2680	2900	4080	46	52
		2	1.80		40	110	90	215	200	420	370	450	20	125	260	750	1030	1750	2160	3020	3480	3850	19	65	
		3	1.80	20		70	50	135	125	200	350	380	355	15	55	320	470	950	1270	2220	2790	3400	4220	33	49
		4	1.80		35	90	150	170	295	275	430	445	40	45		680	210	1480	2060	2430	4720	4290	53	38	
		5	1.80		40		135		265		440		335		160		1220		2180		3460		3740		14
6		1.80	40	45	55	70	75	110	145	160	185	195	170	180	350	570	610	890	1270	1500	1520	2510	(⁴)	24	
35-55 μ	1	1.80					45	45	100	240	315	365	10	25	110	230	400	505	1220	1610	2590	3520	41	50	
	2	1.80			30		65	45	115	260	320	380		35	105	355	615	875	2160	2360	2940	3500	25	47	
	3	1.80			35		25	75	30	115	175	300	360		20	105	145	765	605	2265	1810	3070	3380	36	36
	4	1.80				30	55	55	145	155	310	370		20	5	200	20	515	1580	1280	4320	2980	45	23	
	5	1.80				30		105		315		335		55		490		1070		2560		2540		17	
>35 μ	6	1.80		25		35	40	65	80	180	175	40	50	80	140	110	180	210	370	580	1130	(⁴)	(⁴)		

The concrete cylinders made from the three fractions of material finer than 35 microns had smooth glossy surfaces in all cases where the mix had remained workable until the molding was completed. On the other hand, the cylinders made from the two largest sized fractions always had rough surfaces and appeared to be much more porous. When the wet concretes made from the 22-35 and 35-55 fractions were being tamped into the molds a considerable layer of water would usually rise to the surface. Although the water in all cases had been taken up into the body of the specimens before the twenty-four hour tests were made, its occurrence might give rise to some question as to whether the cement-water ratio for these specimens actually was the ratio of the weights of cement to water in the concrete mix or whether the concrete was of a higher ratio and contained a certain amount of absorbed water. The analysis of the data, which will follow, indicates that these differences in ability to hold water did not change the "effective" cement-water ratios appreciably.

The concrete mix of the I blend was always rather wet, while that of the H blend was always somewhat dry and hard to work. Since the mixes of the I blend showed signs of water segregation in only two cases and could always be molded into good cylinders, the strength data obtained for this blend should not be open to much criticism. The concrete mixes of the H blend, however, in the majority of cases were sufficiently stiff to leave some room for question as to the compactness of the cylinders molded therefrom, even when there was no noticeable honeycombing. The cylinders made from the H blend usually did not have as smooth glossy surfaces as those made from the other three blends.

In addition to the variations in working qualities resulting from size gradation described in the above paragraphs, there were also variations peculiar to individual cements. The fine fractions and higher-surface blends of ground clinkers nos. 2 and 3, without the addition of gypsum, tended to stiffen immediately after the mixing was completed and the cylinders molded from them showed considerable honeycombing. The coarser fractions and lower-surface blends of these cements, however, were not as much affected by the tendency to stiffen and usually molded into good cylinders. A direct comparison of the strengths in these instances, therefore, would be unfair to the finer fractions and the two fine blends. The same tendency was shown by the high-early-strength clinker, no. 5, even after the addition of 3.6 percent of gypsum. For this brand it was necessary to add 10 percent of gypsum to the 0-7 fraction and 6.5 percent to the H blend in order to obtain cylinders free from honeycombing with the regular 1.25 and 1.80 cement-water ratios, respectively.

In this connection the N and O blends, which appear at the bottom of table 4 but have not been previously mentioned, might be discussed. In designing the mortars and concrete mixes from which the test specimens labeled N and O, respectively, were fabricated an attempt was made to use the weights of blends G and H, which would give the same total cement surface in the resulting mixes as that contained in the I-blend mixes. Thus, while both the N and O mixes contained the same total cement surface as the blend I mixes, they actually contained much less cement by weight. On the average the N mixes contained about 55 percent and the O mixes about 45 percent by

weight, of the cement contained in the blend I mixes. The exact proportions to be used in each instance were calculated from the specific surfaces as determined in the Wagner turbidimeter. It was believed that these tests might yield some direct evidence as to the relation between specific surface and strength. However, in order that comparable figures might be obtained, it was essential that the same cement-water ratios should be used for these mixes as for the four blends, and this requirement led to difficulties. The amount of cement was so much decreased in proportion to the aggregate that the quantity of water required by the regular ratio was not sufficient to produce a workable mix. The mortars and the concrete mixes were in all cases of about the consistency of moist earth and there was but very little cohesion. The concrete cylinders had very rough surfaces and were obviously not compact. It is possible, therefore, that the results obtained from these mixes do not have much quantitative significance, but they do indicate certain trends in a qualitative way, which will be subsequently considered.

Since only three strength specimens were tested at each age it was not possible to obtain any very exact measures of the precision of the strength determinations. The "standard deviation" of the mean of three values as given by the formula

$$\sqrt{\frac{v^2}{n(n-1)}}$$

where v is the deviation of an observation from the arithmetical mean and n is equal to the number of observations, or 3 in this case, was calculated for the compressive strengths obtained at the ages 1 day, 7 days, and 1 year in all tests of cements 1 to 4, inclusive. The values obtained, expressed as percentages of the strengths, ranged from 2.3 to 6.0 with averages of 4.8, 4.1, and 4.4 for the ages 1 day, 7 days, and 1 year, respectively.

If the factors considered above are borne in mind, an examination of the data in table 4 will bring out a number of generalities. In the first place it can be seen that the strengths are closely, although not directly, related to specific surface. The relation is much more distinct at the early ages than at the latter. This, of course, is as would be expected since the rate of reaction must be closely related to the surface area in contact with the water, and as the reaction proceeds the effective surface areas change. The relation will be further considered in the theoretical discussion.

Another effect which is easily noticed is that produced by the addition of gypsum to the clinker. The strengths were, in general, considerably increased by this addition, particularly at the early ages. The 0-7 fraction is an exception to the rule, because in almost all instances the strength of this material shows a decrease after the gypsum has been added. Another exception to the rule is found in the case of clinker no. 4. The addition of gypsum caused a large increase in all of the strengths at the early ages, but at the age of one year, and even at 28 days for the blends, the compressive strengths of the plain ground-clinker specimens were considerably higher. The order of the tensile strengths remained unchanged.

The correlation between tensile and compressive strengths is as good as might be expected. The same general tendencies are exhibited by each group of data. The falling off in one-year tensile strength is a common occurrence with tensile specimens stored in water.

2. THEORETICAL CONSIDERATIONS

The question that has probably been the subject of the most controversy in discussions of the effect of fineness on strength pertains to the importance of the very finest material, or the "flour", as it is sometimes called. Several investigators have studied fractions of the finest material, such as that finer than 5 or 10 microns, but in testing these fractions they have always had to use more water than in the whole cements or the coarser fractions, and therefore have been unable to obtain comparable results. The same difficulties were encountered in this investigation. Several attempts were made at testing the 0-7 and 7-22 fractions with the same water ratio, but it was not possible in any case to obtain good specimens for both materials.

The results of some of the attempts made at reaching a compromise are shown in table 4. In the case of cement no. 1 it is seen that the strengths of the 0-7 are considerably higher at 7 and 28 days with the cement-water ratio of 1.55 than with the regular 1.25 ratio. They show still higher strengths with the ratio 1.80, although this mix was so dry when molded that it was difficult to see how the specimens could develop any appreciable strength. The data available on cement no. 2 probably illustrate the effect better than those of any of the others. Here three intermediate water ratios were tried. The strengths increase regularly up to the ratio 1.65, when they begin to fall off. The cylinders made with this highest ratio were very badly honeycombed, and it was rather surprising that they developed as high strengths as they did. With cement no. 5 an attempt was made to use the same intermediate ratio for both the 0-7 and the 7-22 fractions. The strengths of both fractions were lowered considerably, the 7-22 remaining the higher. This, however, was not a fair test, because the fine fraction of no. 5 heated up and became dry even with the 1.25 cement-water ratio, and when the water was decreased it became so dry that there was practically no cohesion at all. When tests were made on the 7-22 fraction of cements 3, 4, and 5, using the same amount of water as was used on the 0-7 material, the strengths developed in most instances were less than half as high as those which were obtained with the higher ratio, although in every instance there had been a considerable amount of water at the tops of the cans, even at 28 days, so that the "effective" ratio really was higher than 1.25.

If we assume that the relation between the cement-water ratio and strength is one which approximates a straight line and extrapolate to the ratio 1.80, we see that the fine material has a very high potential strength. It is known that for ordinary cements the strength is very nearly directly proportional to this ratio, within the workable range, so that there is some justification for such a procedure. There are not enough points within the workable range to establish a line, but it can be seen that the strengths increase rapidly with increasing cement-water ratio, until the point is reached where the effect of poor fabrication becomes apparent. All the evidence from these tests,

therefore, points to the conclusion that the 0-7 micron material has a very high intrinsic worth as far as strength conferring properties are concerned.

There is still another and entirely different way in which the problem may be approached on the basis of the data in table 4. If we assume that the contributions of the individual fractions to the strengths of the blends are additive, it is possible to arrive algebraically at the "apparent strength" of the fine fraction. Thus if *a, b, c, d,* and *e* are the strengths of the five fractions of a given cement and *f, g, h,* and *i* are the strengths obtained by the blends, we can write down the equations

$$P_{(0-7)F}a + P_{(7-22)F}b + P_{(22-35)F}c + P_{(35-55)F}d + P_{(>55)F}e = 100f$$

$$P_{(0-7)G}a + P_{(7-22)G}b + P_{(22-35)G}c + P_{(35-55)G}d + P_{(>55)G}e = 100g$$

where the *P*'s refer to the percentages of the fractions in the blends. For example $P_{(0-7)F}$ represents the percentage of the 0-7 material contained in blend F. These equations should hold if the above assumption is sound and if all the fractions had been tested in the same way. Since four of the fractions were tested under similar conditions, we can, by proceeding on this assumption, use these equations to calculate the contribution of the 0-7 fraction to the strengths of the blends. The equations are then written:

$$a = \frac{100f - P_{(7-22)F}b - P_{(22-35)F}c - P_{(35-55)F}d - P_{(>55)F}e}{P_{(0-7)F}} \text{ etc.,}$$

Apparent compressive strengths have been calculated according to this method and are presented in tables 5 and 6. Table 5, which is a tabulation of the seven-day strengths as calculated from each of the blends, is included in order to give an idea of the kind of agreement found between the four different values which it was possible to calculate for each age. Table 6 is a summary of the calculated strengths. The values presented in table 6 are the weighted means, or the most

TABLE 5.—Calculated compressive strength of 0-7 micron fraction at seven days

Cement no.	Strength in lb/in. ² calculated from strength of blends				
	F	G	H	I	Arithmetic mean
1 { No gypsum.....	4900	5770	4450	4000	4780
{ Gypsum.....	6735	5240	4270	5470	5430
2 { No gypsum.....	4850	4920	3830	3740	4340
{ Gypsum.....	4275	4330	3400	4120	4030
3 { No gypsum.....	3600	3810	2840	3890	3540
{ Gypsum.....	3460	4130	4640	5000	4310
4 { No gypsum.....	2425	3420	3080	1580	2630
{ Gypsum.....	850	2760	3150	1240	2000
5 Gypsum.....	4420	3270	3810	3920	3860
6 Gypsum.....	2000	3000	3190	1430	2400

TABLE 6.—Probable means of compressive strengths (lb/in.²) of 0-7 fraction as calculated from strengths of blends, F, G, H, and I

Cement no.	Strength at various ages (with, G, and without, NG, gypsum)									
	1 day		3 days		7 days		28 days		1 year	
	NG	G	NG	G	NG	G	NG	G	NG	G
1.....	270	990	3160	3780	4810	5150	5430	3800	5010	4060
2.....	420	880	2740	2830	4290	3880	4700	4200	4800	4260
3.....	340	740	2620	3040	3330	4300	2590	4640	3470	3970
4.....	-----	680	1700	1580	2880	2390	4540	3720	4130	3950
5.....	-----	590	-----	2130	-----	3820	-----	4150	-----	4160
6.....	-----	1160	-----	1800	-----	2720	-----	4990	-----	5980

probable means of the four calculated values. The arithmetic means do not represent the best values because the strengths as calculated from any two different blends are susceptible of quite different errors. The standard deviation of each calculated value was obtained roughly by assuming a standard deviation of 5 percent in all of the strength determinations, calculating the averages of the standard deviations of the strength determinations for each age in pounds per square inch from the averages of all the compressive strengths for that age, and making use of the general equation

$$(du)^2 = \left(\frac{\delta u}{\delta a_1} da_1\right)^2 + \left(\frac{\delta u}{\delta a_2} da_2\right)^2 + \dots,$$

where

$$u = f(a_1, a_2, \dots),$$

and du is the standard deviation of u brought about by the joint occurrence of the errors da_1, da_2, \dots . The standard deviations so calculated are given in table 7. The values given in table 6 were obtained by weighting each strength value, as calculated, by the reciprocal of its standard deviation squared, and thus calculating the weighted mean, or the most probable mean, of the four values. The figures given in table 7 are not measures of the actual precision of the calculated values and should be considered only as indicating the relative precision of the four values calculated for any one age.

The manner of increase with age and also the actual magnitude of the calculated strengths given in table 6 suggest that these values are possibly good measures of the actual contributions of the 0-7 micron material to the strengths of the blended cements. One would expect the 0-7 fraction to be almost completely hydrous at the end of 7 days. In most instances the calculated strengths do not show very large increases after 7 days, although the blended cements increase considerably in strength between 7 and 28 days. At 1 year the calculated strengths of the 0-7 are on the average about equal to the observed strengths of the 7-22 fraction, and this is what would be expected since both materials should be very nearly completely hydrous at this age. In any case it seems logical to believe that these calculated strengths indicate the actual worth of the fine material much more closely than the strength data obtained with the low cement-water ratio. Further evidence pointing to this conclusion will be brought out by an attempt to find a direct relation between strength and some function of particle size distribution.

TABLE 7.—Standard deviations of calculated strengths of 0-7 micron fraction

Age	Standard deviation in lb/in. ² of value calculated from blend			
	F	G	H	I
1 day.....	70	85	80	95
3 days.....	250	295	210	390
7 days.....	450	430	310	660
28 days.....	650	580	390	1,060
1 year.....	930	720	430	1,560

The best-known function of size distribution is surface area per unit weight, or specific surface. The belief was once held quite generally that strength at any given age was very nearly a direct function of the original specific surface of the cement. The results of this and other investigations show that if both fractions and blends are considered this relation holds approximately only for the very early ages.

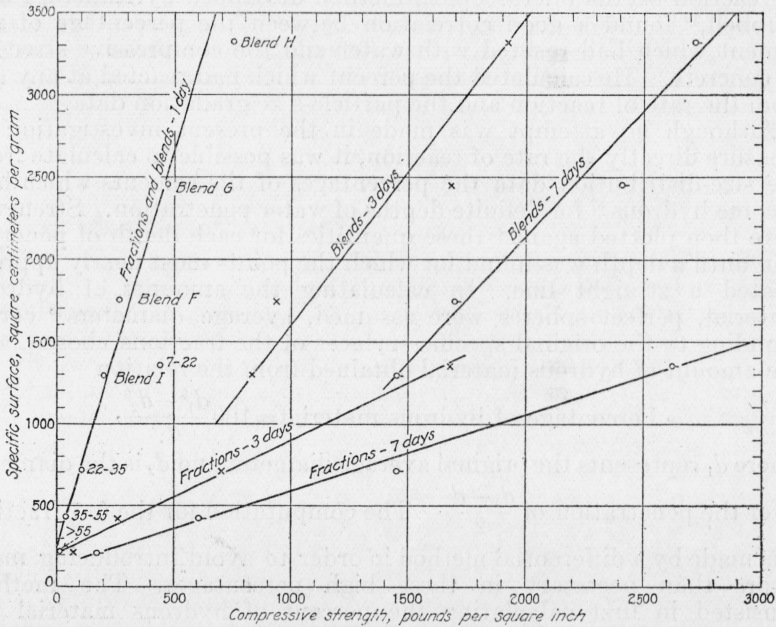


FIGURE 7.—Averages of compressive strengths of fractions and blends of six cements as a function of specific surface.

In figure 7 the averages of the compressive strengths for the ages 1 day, 3 days, and 7 days are plotted against specific surface. At the age of 1 day it is possible to visualize a single line through the points. At 3 days the points are much more scattered and the possibility of two distinct curves is suggested. At 7 days it is clearly seen that two distinct curves are obtained, one for the blends and one for the individual fractions. A little consideration will show that this is what would be expected. The rate of reaction must at all times be closely related to the surface of the anhydrous material in contact with the

water. At the age of 1 day the water has not yet penetrated very deeply and the effective specific surfaces have not been appreciably changed so that the strength is very nearly directly proportional to the original specific surface. However, at 3 days much of the fine material in the blends has been rendered completely hydrous so that the effective specific surfaces and therefore also the rates of reaction of the blends have decreased considerably, while the fractions, not containing any fine material, are still being used at a rate not much reduced from the original. This is quite likely the explanation of the fact that the 7-22 fraction, for instance, shows a higher strength at 3 days than blend F, although the original specific surface of the fraction is lower than that of the blend. The same effect, of course, is further accentuated at 28 days.

This explanation of the failure of specific surface to show a direct relation to strength immediately suggests another possible function of gradation. If the rate of strength development is related to the rate of reaction, the strength at any age must be related to the percentage of hydrous material at that age. Eiger,¹⁵ measuring the rate of reaction by the microscopical method developed by Anderegg and Hubbell,¹⁶ found a good correlation between the percentage of the cement which had reacted with water and the compressive strength of concrete. He calculated the percent which had reacted at any age from the rate of reaction and the particle-size gradation data.

Although no attempt was made in the present investigation to measure directly the rate of reaction, it was possible to calculate from the size-distribution data the percentages of the cements which had become hydrous¹⁷ for definite depths of water penetration. Strengths were then plotted against these quantities for each depth of penetration until a depth was found for which the points most nearly approximated a straight line. In calculating the amounts of hydrous material, perfect spheres were assumed, average diameters¹⁸ corresponding to the original specific surfaces of the fractions chosen, and the amount of hydrous material obtained from the relation

$$\text{Percentage of hydrous material} = 100 \frac{d_1^3 - d_2^3}{d_1^3},$$

where d_1 represents the original average diameter and d_2 is the diameter after the penetration of $\frac{d_1 - d_2}{2}$. The computation for the 0-7 fraction

was made by a differential method in order to avoid introducing more errors than necessary in these high percentages. The method consisted in first calculating the percent of hydrous material for a penetration of one-tenth micron, then taking a new average diameter and finding the percentage of the remainder, which became hydrous during another tenth-micron penetration, calculating the new remainder, and continuing the process to the desired depth. The values for the blends were obtained directly from those of the fractions by calculation from the percentage compositions.

Table 8 gives the calculated percentages of hydrous material for six depths of penetration, and in figures 8 and 9 the 7-day tensile and

¹⁵ A. Eiger, *Tonind. Ztg.* 56, 532, 558 (1932).

¹⁶ *Proc. Am. Soc. Testing Materials* 29, II, 554 (1929).

¹⁷ By hydrous material is meant that portion of the cement into which water has penetrated without any implication as to the progress of the resulting chemical reactions or the composition of the resulting products.

¹⁸ See footnote to table 8.

compressive strengths of cement no. 2 are shown plotted against the values calculated for a penetration of 1.5 microns. Cement no. 2 was chosen because of the uniform compound compositions of the fractions. Some of the other cements show better relationships at this age. For instance, the 7-day tensile and compressive strengths of cement no. 1 show much smaller deviations from straight lines when plotted against the hydrous material for a penetration of 1.5 microns. At 3 days the correlations are in general better than at 7 days, and the compressive strengths of cement no. 2 for this age show a very good relationship to the calculated values for a penetration of 1 micron. At ages later than 7 days the points are much more scattered, due possibly to larger deviations entering into the strengths themselves as well as to the necessarily increasing errors in the calculated percentages of hydrous material, but the tendency towards straight line relationships remains apparent. The averages of the 28-day compressive strengths of the six cements correlate very well with the calculated values for a penetration of 4 microns, as can be seen in figure 9.

TABLE 8.—Calculated amounts of hydrous material

Fraction or blend	Percentage hydrous for penetration of					
	0.5 μ	1 μ	1.5 μ	2 μ	4 μ	10 μ
0-7 μ	61	87	97	99	100	100
7-22 μ	20	36	50	61	92	100
22-35 μ	11	20	29	37	65	98
35-55 μ	6	13	18	24	44	83
>55 μ	3	6	10	13	24	52
F.....	20	33	41	47	65	87
G.....	28	44	54	62	81	96
H.....	36	55	65	71	86	98
I.....	16	27	34	40	60	82

NOTE.—The diameters used in making the calculations were 3.5, 14, 27, 45, and 91 microns for the 0-7, 7-22, 22-35, 35-55 and <55 fractions, respectively. These values were obtained by substituting the specific surface as calculated from microscopical distribution counts for ss in the equation

$$d = \frac{19050}{ss},$$

where ss is the surface in cm^2 of 1 gram of particles of diameter d microns and density 3.15, and 19050 is a constant, which is equal to the surface in cm^2 of 1 gram of spherical particles of diameter 1 micron and density 3.15. This diameter, which might be termed the "equivalent-surface" diameter, is also given by the equation

$$d = \frac{\sum nd^3}{\sum nd^2},$$

where n is the number of particles of diameter d microns in the representative slide.

A comparison of figure 7 with figures 8 and 9 shows that the percent of hydrous material, or, if more rigor be desired, the function of particle-size distribution, which has been called "percent of hydrous material", is a much more fundamental function than the specific surface insofar as strength relationships are concerned. Whereas the strength is closely related to specific surface only when but one type of distribution is present, it is directly related to the new function regardless of the kind of distribution. The fact that the strengths of the fractions fall on the same line as those of the blends tends to prove that the calculated quantities are at least proportional to the amount of hydrous material. There must be some physical cause

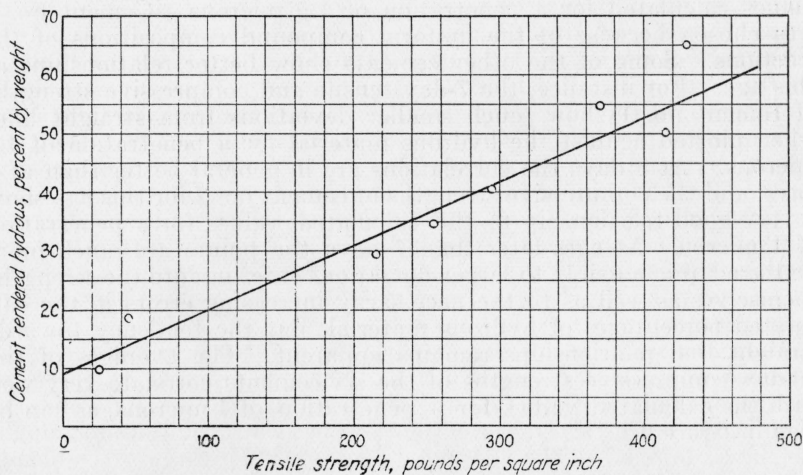


FIGURE 8.—Tensile strengths of fractions and blends of cement no. 2 at 7 days as a function of the percent of the cement rendered hydrous by a water penetration of 1.5 microns.

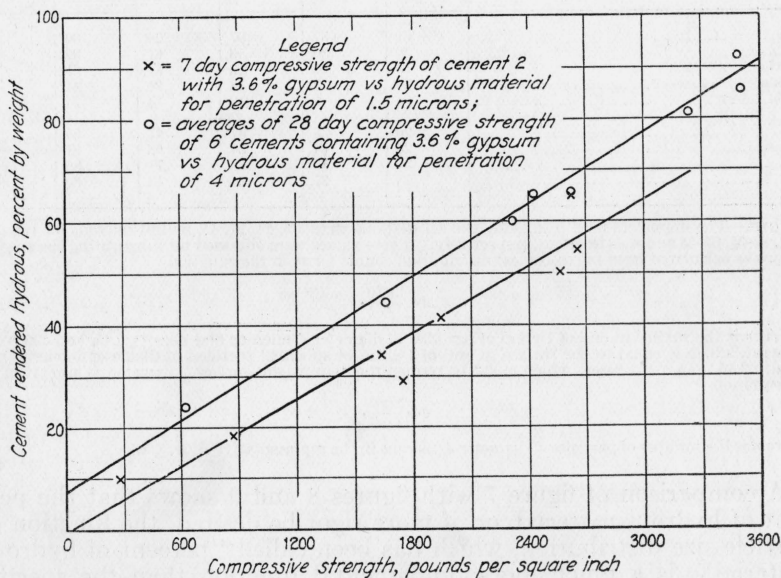


FIGURE 9.—Averages of 28-day compressive strengths of both fractions and blends made from the six cements as a function of the percent of cement rendered hydrous by a water penetration of 4 microns, and the 7-day compressive strengths of fractions and blends made from cement no. 2 as a function of cement rendered hydrous by a water penetration of 1.5 microns.

underlying a relationship so fundamental and it is logical to suppose that strength is proportional to the hydrous material. It is interesting to note in this connection that the calculated "apparent strengths" of the 0-7 fraction in most cases come very close to falling on the hydrous material versus strength line, thus affording additional proof of the validity of the assumptions made in each instance.

It is possible to deduce several postulates from the fact that the strengths are related to the calculated percentages of hydrous material. For one thing it shows that the size distribution of the cement particles, of itself, has very little to do with the strength of concrete. A fraction containing only particles within a narrow size range will produce the same strength of concrete as a whole cement containing all sizes of particles if the amount of hydrous material is the same in each instance.

Another possible deduction is that the 0-7 fraction has the same intrinsic worth as any other. It has been maintained by some investigators that particles below a certain size, such as 4 microns, are of no value; but if this had been the case the relationships found would not have obtained. The amounts of hydrous material for the blends were deduced by summing up the contributions of the individual fractions, allowing weights in proportion to the volume for particles of all sizes, and since the 0-7 fraction usually contributed the most to this sum, the fact that the strengths of the blends did fall on the line shows that all of the 0-7 micron particles must have contributed to the strength according to their sizes. The 0-7 fraction contributes more to the strength of concrete, at least at the early ages, than any of the others by virtue of the fact that all of the particles become completely hydrous in a very short time.

From the fact that the amount of hydrous material for the blends of any one cement was obtained by taking the sums of the products of the values for the fractions and the percentages of the respective fractions in the blends, together with the fact that the amount of hydrous material was found to be proportional to the strength, it follows that the strength values are also additive, as was originally assumed in calculating the "apparent strengths" of the 0-7 fraction.

It, of course, must be kept in mind that the conclusions and deductions drawn from this analysis are to be accepted only with reservations. The authors do not insist that the actual amounts of the cements which had become hydrous were equal to those which were calculated and plotted against the strengths. The calculated quantities are rough approximations of the amounts of cement which would have been rendered hydrous by a uniform water penetration of all particles to the assumed depth. The fact that these quantities show direct relations to the observed strengths indicates that they are probably good approximations of the actual amounts of hydrous material. It is realized that other factors might have contributed to bring about this observed relationship. It might also be pointed out that these conclusions apply only to the results of these particular tests as made. Whether or not they would apply for different storage conditions or for tests made with different mixes or cement-water ratios is a matter for conjecture.

The data from the N and O mixes were not used in any of the calculations or correlations. Only a brief inspection is necessary to

show that these data fall in a class by themselves and would not have fitted in with the other data. For example, the compressive strength of the N cylinders at 28 days should have been about 55 percent of that of the G-blend cylinders in order for the strength to be proportional to the hydrous material; actually the averages of the N and G compressive strengths for all six cements were 1,080 and 3,240 pounds per square inch, respectively. Likewise, the O mix yielded concrete, on the average, of only 20 percent of the strength of the H-blend concrete at 28 days, although the percentage should have been about 45 according to the proportionality requirement. It would seem that these large discrepancies must be attributed to the poor working qualities of the N and O mixes, which made it impossible to mold good test specimens. The strength of concrete could be expected, logically, to be closely related, within a certain range, to the weight of cement in the concrete mix, if the cement-water ratio were kept constant. As the proportion of cement and water is reduced, however, a point must necessarily be reached where all semblance of proportionality between amount of cement and strength must cease to exist. The tensile- and compressive-strength data of the N and O mixes, taken together, serve to illustrate this idea. The proportions, by weight, of cement to sand in the N and G mortars were 1:5.4 and 1:3, respectively. The proportions, by weight, of cement to total aggregate in the N and G concrete mixes were 1:11.9 and 1:6.6, respectively. The N tensile strengths are on the average very nearly equal to 55 percent of those of the G blend, while the N compressive strengths are only about 30 percent of those of the G blend, as indicated above. It therefore seems possible that, while the proportion of aggregate to cement in the concrete mixes was made too high, the proportion of sand to cement in the mortars was not so great as to render the supposed relationship between strength and amount of cement invalid. The existence of a critical point in this relationship is further suggested by the fact the O tensile strengths, on the average, are considerably less than 45 percent of those of the H blend.

When the N and O strength data are compared to those of blend I, some peculiarities are found which are not easily explained. The N and O test specimens theoretically contained the same total cement surface as the I specimens and might therefore have been expected to show about the same 1-day strengths. Actually, almost all of the N and many of the O 1-day strengths are considerably higher than those of blend I. It is possible that the reduction of the proportions of cement to aggregate may have had the effect of changing the cement-water ratio so as to make the "effective ratio" higher than the actual ratio of the weight of cement to that of water, although allowance was made in designing the mixes for absorption by the aggregate.

As an appendix to the foregoing discussion, there are certain mathematical deductions which might be added because of their interest as *curiosa* rather than for any direct bearing which they might have upon the problem in hand. If we assume a spherical cement particle of radius r and let it be uniformly hydrous to a depth such that the radius of the anhydrous material will have been reduced

from the original by the amount x , we can express the decimal part by weight which has become hydrous as equal to

$$\frac{r^3 - (r-x)^3}{r^3}$$

Calling this part H and differentiating with respect to time, we obtain the equation

$$\frac{dH}{dt} = \frac{3}{r^3} (r-x)^2 \frac{dx}{dt} \quad (1)$$

This equation shows that the rate of becoming hydrous, $\frac{dH}{dt}$, of a spherical particle of radius r at any time, t , is dependent upon the linear rate of advance of the hydrated film, $\frac{dx}{dt}$, and upon the depth of penetration, x . If x and $\frac{dx}{dt}$ were known for any time, t , it would be possible to calculate the rate of change to the hydrous state for that time by means of the above equation.

The data on four cements published by Anderegg and Hubbell¹⁹ show that these particular cements, as tested, hydrated in such a way that the depth of penetration became a linear function of the logarithm of the time after 7 days. For example,²⁰ the relationship between penetration and time for their portland cement "A", with no gypsum addition, can be very nearly expressed by the relation

$$x = 3 \log_{10} t, \quad (2)$$

when x is the depth of penetration in microns and t is the time of hydration in days. This relationship very nearly obtained for five ages, from 41 hours to 270 days, at which hydration measurements were made. Differentiating this expression with respect to time, we get

$$\frac{dx}{dt} = \frac{1.31}{t}$$

and substituting for x and $\frac{dx}{dt}$ in equation 1, we have

$$\frac{dH}{dt} = \frac{3.93}{r^3 t} (r - 3 \log_{10} t)^2 \quad (3)$$

From this equation the rate at which a particle of radius, r , was being hydrated at any time, t , can be calculated. For instance, at the ages 2, 3, 7, 28, and 180 days, respectively, a 20 micron diameter particle was being used at the rates 16.3, 9.6, 3.1, 0.4, and 0.023 percent per day. By letting $x=10$ in equation 2 we can find the time at which a spherical 20-micron particle would become completely hydrous on the assumption that the same relationship obtained throughout between penetration and age. Doing this, we find t equal to 2,150 days, or 5.9 years. Thus, although this particle is approximately 99 percent hydrated at the end of 1 year, 5 more years are required for the reaction to go to completion if the relation between rate of hydration and time remains the same.

¹⁹ Proc. Am. Soc. Testing Materials 29, II, 554 (1929).

²⁰ This cement was chosen because of the simplicity of its equation; the equations for the other cements all contain a constant term.

3. PRACTICAL CONCLUSIONS

A discussion of the effect of fineness of grinding of cement on the properties of concrete, if precedent be followed, perforce should contain some mention of "optimum gradation." This concept of a cement having the best possible gradation for strength purposes, and at the same time one which would yield workable concrete mixes, has been much talked of by past investigators and commentators. It would seem from the results of this investigation that the gradation which would satisfy both of the above requirements really would not be a "gradation" at all in the usual sense of the word, because the particle sizes would have to be restricted to a relatively narrow range.

A cement containing about 70 percent of material between 10 and 20 microns and the remainder less than 10 microns should produce a concrete of almost as high early strength and a higher ultimate strength than any cement graded so as to contain an appreciable amount of material coarser than 20 microns, and it should also yield workable concrete mixes. This cement would have about the same specific surface as blend G and should therefore have about the same 1-day strength, while at the later ages it should develop higher strengths because it would become completely hydrous in a much shorter time. Blend G contained 25 percent of 22-35 micron material and 13 percent of material greater than 35 microns, but on the average the 22-35 fraction only developed about 70 percent at 28 days and 95 percent at 1 year of the strength developed by the 7-22 fraction at the same ages, and the 35-55 fraction was only about 75 percent as strong as the 7-22 at 1 year and less than 50 percent as strong at any of the earlier ages. It is therefore logical to believe that a cement containing only material finer than 20 microns in size would have developed considerably higher strengths than blend G.

In such an "optimum" cement it would appear inadvisable to increase the quantity of 0-7 fraction much above that used in blend G, or 30 percent. Blend H, which contained 47 percent of this fine material, produced cylinders which were honeycombed in some cases and of doubtful compactness in others. Although these cylinders were stronger at early ages, at 1 year they were weaker than the more compact cylinders of blend G. In actual practice it would have been necessary to use a lower cement-water ratio for blend H, and a lower ratio would quite likely have yielded concrete of lower strength. This belief is supported by the results obtained in studying the effect of varying cement-water ratio on the strength of the 0-7 micron fraction. In order to prove that there is a practical limit to specific surface, beyond which no improvement in strength could be attained, it, of course, would be necessary to establish the relations between cement-water ratio and strength for the higher surface blends by actual test.

For the ordinary types of gradation, obtained by commercial grinding, it would seem that there is no such thing as an "optimum." The distribution curves are automatically quite similar, and the most suitable type would be determined by the strength to be required of the concrete. The more finely the cement is ground, within practical limits, the higher will be the early strength, and possibly also the ultimate strength of the concrete. It seems very probable that the hydration process would become arrested, or, at least, very much

retarded, after a short length of time under conditions of practice when the water might escape from the concrete. Under such conditions it would seem desirable to use a cement of high specific surface in order that as much hydration as possible could take place before the reaction became arrested.

The strengths of the concretes made from the blended cements in this investigation were closely related to the specific surface at all ages tested, and it therefore seems that the specific surface is a sufficiently good criterion of strength for practical purposes. If cements having more irregular distribution curves were to be produced, it would probably be advisable to adopt some sort of fineness modulus based upon the amount of hydrous material for different depths of water penetration.

VI. SUMMARY

Five laboratory ground clinkers and one commercial cement have been separated into size fractions, and studies have been made of neat pastes, mortars, and concretes prepared from the fractions as well as from four different blends. The ground clinkers were separated into the five fractions 0-7, 7-22, 22-35, 35-55, and >55 microns. The cement was separated into only four fractions, no separation being made of the material coarser than 35 microns. The four blends ranged in specific surface from about 1,300 to 3,300 cm²/g. Most of the tests were made both with and without the addition of gypsum.

The fractions of any one cement in most cases showed considerable variations in chemical composition and calculated compound composition. The tricalcium silicate, in general, tends to be more concentrated in the finer sizes, while the higher percentages of dicalcium silicate usually occur in the coarser fractions. The other constituents are about equally distributed.

It was found that all of the fractions, with the exception of the fine 0-7 micron material, were more or less deficient in the power to hold water and that they were lacking in plasticity and good working qualities. These characteristics ranged from the 7-22 micron fraction, which was not vastly different from a whole cement, to the coarsest fraction which behaved very much like a fine sand. The 0-7 micron fraction was very plastic, had a high water-retaining capacity, and was also characterized by an extreme stickiness.

The working qualities of the blends ranged from the coarsest blend, which was possibly somewhat more harsh than the average commercial portland cement, to the highest surface blend which was more plastic and required more water than the ordinary high-early-strength cement. It was found that on the average the amount of water necessary for normal consistency was very nearly a direct function of specific surface. Also, the time of initial set was found to be very closely related to surface.

At one day it was found that strength is directly related to specific surface for both the fractions and the blends. At other ages when strength was plotted against specific surface one line was obtained for the fractions and another for the blends. The strengths of the blends were closely related to specific surface at all ages.

Some good correlations were obtained between strengths and the percentage of hydrous material corresponding to definite depths of water penetration as calculated roughly from the size-distribution

data. The fact that the strengths of the fractions when plotted against the percentage of hydrous material fell on the same lines as those of the blends showed the relationship to be of a more fundamental nature than that existing between specific surface and strength.

Since a much lower cement-water ratio had to be used in molding the strength specimens from the 0-7 micron fraction than in molding those of any of the other fractions or the blends, the strength data obtained for this fine material were not directly comparable with those obtained for the other fractions or the blends. However, the strength of this fraction was calculated from its contribution to the strengths of the blends and these calculated strengths were found to be greater at the early ages than the observed strengths of any of the other fractions and at least as great at the later ages.

Acknowledgment is made to P. H. Bates for valuable suggestions offered during the planning and progress of this investigation. The photomicrographs of the fractions were made by Herbert Insley.

WASHINGTON, February 8, 1935.