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PHASE I: ENERGY-CONSERVATION POTENTIAL OF
PORTLAND CEMENT PARTICLE-SIZE-DISTRIBUTION
CONTROL

Final Report, March 1979

By
R. A. Helmuth

MASTER

March 1979

Work Performed Under Contract No. EC-77-C-02-4269

Construction Technology Laboratories
A Division of the Portland Cement Association
Skokie, Illinois

U. S. DEPARTMENT OF ENERGY

Division of Industrial Energy Conservation

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Submitted by

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Project Manager

Report to

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March 1979

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ABSTRACT

The properties of cements with carefully controlled particle size distributions were compared with those of normally ground cements having a Blaine fineness of about $3600 \text{ cm}^2/\text{g}$. Progressive reduction of the maximum particle size to 20 microns improved strength development. Further reduction to about 14 microns decreased rather than improved strength development.

Some of these particle size controlled cements produce as high, and often much higher, strengths at ages from 1 to 60 days at Blaine finenesses 450 to $800 \text{ cm}^2/\text{g}$ lower than the normal grinds of the same composition. The cements with 20 micron maximum size particles can have finenesses as low as $2800 \text{ cm}^2/\text{g}$, whereas with larger particles, higher specific surface areas are required for equal strengths. The improved strengths were a result of more rapid and more complete hydration of the cement. Variations of clinker composition did not significantly alter these conclusions.

Drying shrinkage of the particle size controlled cements was in some cases less than for normally ground cements. They also performed better than normally ground cements over a wide range of mixing and curing temperature (42°F to 100°F).

Direct energy conservation of 27% in finish grinding and 8.5% in more efficient utilization of the cement is estimated to result from the use of particle size controlled cements. For a U.S. production of 75 million tons, this corresponds to conservation of 9.5 plus 37, i.e., 46.5 trillion Btu/year.

CONTENTS

	<u>Page</u>
1. Introduction and Summary	1
2. Cement Clinker Selections	5
3. Preparation of Cements	7
3.1 Gypsum Preparations	8
3.2 Normally Ground Clinkers	9
3.3 Particle Size Controlled Clinkers	9
3.4 Blending the Ground Clinker with Gypsum	11
4. The Effects of Gypsum Fineness	12
4.1 Series I test results	12
4.2 Series II Preliminary Tests	15
4.3 Additional tests of paste flow properties	16
4.4 The effect of gypsum fineness on strength	18
4.5 Fineness determinations - which are correct?	20
4.6 Future considerations	22
5. Effects of Large Variations of Particle Size Range and Gypsum Content on Fresh Paste Properties and Strength Development	22
5.1 Series II Preliminary Tests	22
5.2 Series II tests	24
5.3 Discussion of the Series II Results	31
5.4 Analysis of the Water Requirement for Flow	32
5.5 Direct Measurement of the Inactive Water	36
5.6 The Need for Additional Tests	37
6. Effects of Particle Size Ranges on Strength and Drying Shrinkage	38
6.1 Series III Preliminary Tests	38
6.2 Series III a Preliminary Concrete Tests	43
6.3 Series III b Cement Paste Tests	46
Bleeding	47
Workability	48
Degree of Hydration	49
Strengths	50
Gel-Space Ratio and Strength	52
Utilization of the Cement for Strength	54
Drying Shrinkage	56
7. Effects of Mixing and Curing Temperature	58
8. Effects of High-Alkali and High Sulfate Contents in Cement Clinkers	60

CONTENTS (Continued)

	<u>Page</u>
9. Estimates of Energy Conservation Potential of Cement Particle Size Control	63
9.1 Grinding Energy	63
9.2 More Efficient Utilization of Cement	65
9.3 Blended Cements	66
9.4 Other Considerations	67
10. Summary of Conclusions	67
Figures 1-20	
Tables 1-25	

1. Introduction and Summary

The overall objective of this research program was to determine the energy conservation potential of portland cement particle size distribution control. Portland cement manufacture is an energy intensive industry. About 6 million Btu/ton of kiln fuel is used in burning the clinker and about 45 Kwh/ton is used to grind the clinker to make cement. The research was directed towards conservation of this energy usage by developing cements that would perform at least as well as normally ground cements when less finely ground than normally ground cements, and by more efficient utilization of the strength producing potential of the cement clinker by particle size control.

Study of the literature had indicated that considerable potential existed for energy conservation by this means. This was reviewed in the proposal for this work. That study indicated that as much as 20 to 40% of the cement in normally ground cements was not fully utilized for strength development. Our approach was semi-empirical, being assisted by consideration of a simple model of the structure of the fresh cement paste, which determines the physical environment for the hydration reactions and the strength developing structure formation processes during hardening. The model is illustrated in Figure 1. Analysis showed that the largest particles were not fully utilized because they cannot hydrate completely in such dense structures. Also, the fine cement particles in the structure form aggregations which remain as high porosity regions which limit ultimate strength. Hence it appeared that a narrower particle size

distribution was required to more efficiently utilize the cement for strength development. Grinding cements to avoid production of the very fine particles would not only save grinding energy, but should also produce a superior product.

It was also recognized that changing the particle size distribution of the cements would affect all other properties of fresh and hardened concretes. Hence it was important to investigate the water requirement for adequate flow properties, the bleeding capacity, the time of set, and drying shrinkage as well as the strength development. For such cements to be acceptable to users all of these properties must be at least as good as those of normally ground cements. In addition we had to explore the normal range of cement clinker compositions to see how the desired particle size distribution depended on the composition.

The study was begun with an investigation of the effects of the fineness of the gypsum on the properties of cements (Series I) because cements are normally interground with gypsum to control the early reactions of the aluminate phases and to maximize strength development and other properties. It was found necessary to use very finely ground gypsum to duplicate the behavior of interground gypsum.

The next step was to use rather artificial cement particle size distributions to sort out the major effects of reduction of the maximum particle size, and the amounts of the finest material in the 2-5 micron particle size range. Such idealized particle size distribution curves are shown in Figure 2 as

dashed lines for comparison with two particle size distribution curves for normally ground cements of two different Blaine finenesses, which are also shown.

The results of these Series II tests showed the importance of proper control of the amount of 2-5 micron material for control of all properties. Such wide variations in properties occurred with these idealized distributions that it was necessary to conduct additional tests to more closely refine the size distributions before beginning the major Series III tests. The Series II results and the additional tests revealed that the main problem with the particle size controlled cements was their excessive water requirement for flow. The size distributions having good strength development also had high water requirements that would produce fresh concretes of poor workability. This imposed severe limits on the variations that could be used to make cements practical for ordinary use. However, we did succeed in defining size distributions of relatively low Blaine fineness cements that had both good strength development and reasonable water requirements for flow.

In the Series III tests we used several such particle size distributions to explore a narrower range of such distributions with two cement clinkers. These had high and low tricalcium aluminate contents, one of the most important compositional variables in cement clinkers. We found that most of our particle size controlled cements with maximum particle sizes of 30 and 20 microns and various amounts of 2-5 micron material yielded better strengths at all ages (even at one day) than the

normally ground cements despite the fact that they had substantially ($450 - 800 \text{ cm}^2/\text{g}$) lower Blaine finenesses. It was found that this is because they hydrate more rapidly and more completely than normally ground cements of higher fineness. We also investigated their drying shrinkage characteristics. We found that although the drying shrinkage was often higher at equal curing times this was mainly because they were more completely hydrated, and also much stronger. Hence their shrinkage cracking tendencies should be less. In some cases the shrinkages were actually less, despite the more complete hydration which indicates that the hardened paste structure has actually been improved with respect to shrinkage.

We then investigated (Series (IV) the properties of these cements when mixed and cured at the temperature extremes of normal use, 42°F and 100°F . We again found that the particle size controlled cements performed better than normally ground cements.

In the final test Series V we investigated the properties of cements made with compositions representative of other raw materials and manufacturing conditions, one with a high-alkali content and one with both high-alkali and sulfate content. The cements made with the high-alkali content clinker showed some expected variation in properties, but again the particle size controlled cements performed better than the normally ground cements.

Finally, we have made some quantitative estimates of the energy usage savings that would accrue from replacement of

normally ground cements by particle size controlled cements if these were universally adopted by U.S. industry. These and other major conclusions are summarized at the end of this report.

2. Cement Clinker Selections

To determine to what extent the effects of cement particle size distribution control depended on the composition of the cement clinkers, four portland cement clinkers were selected. These represent the normal range of chemical compositions that are encountered in practice. Table 1 gives the oxide analyses, potential compound compositions, and phase compositions as determined by QXRD (quantitative X-ray diffraction analysis).

Most of the work was done with two clinkers, designated 274 and 275, which have relatively low alkali and sulfate contents. They differ mainly in their tricalcium aluminate (C_3A) contents^(a). For normally ground cement, gypsum is added for control of the early hydration reactions so that normal setting, maximum rate of strength development, and maximum drying shrinkage occurs. The optimum gypsum content depends mainly on the C_3A content, and also on the amounts of alkalies and clinker sulfate present. Clinker 274 has a relatively low C_3A content (6.85% potential, 1.88% by QXRD). Clinker 275 has a high

(a) Cement chemist's notation is used for the cement compounds:

C = CaO
S = SiO₂
A = Al₂O₃
F = Fe₂O₃

$\bar{S}$ = SO₃
N = Na₂O
K = Na₂O
 $\bar{C}$ = CO₂

C₃A content (12.11% potential, 7.56% by QXRD). Although the QXRD results are more accurate most workers in the cement industry are more familiar with the potential compound composition computed by the Bogue method as given in Table 1.

In some of the later work two additional clinkers designated 280 and 14K2 were used. Both of these have high alkali contents; 280 also has a high sulfate content. These represent clinkers made from high alkali content raw materials, or with modern preheater kilns which tend to retain more of the alkalies in the clinker, and clinker made with high sulfur fuels. These minor constituents result in the formation of minor phases such as alkali sulfates, anhydrous calcium sulfate (anhydrite), aphthitalite ($K_2SO_4 \cdot Na_2SO_4$) and calcium langbeinite ($2CaSO_4 \cdot K_2SO_4$) which can affect the early hydration reactions and properties of the cement pastes. It was therefore necessary to determine whether the effects of particle size control would depend significantly on these minor constituents.

To be sure that the milling and particle size classification procedures used did not appreciably alter the chemical composition of the ground clinker fractions, several size fractions produced by the Vortec mill and classifier system were chemically analyzed. Results are presented in Tables 2 and 3.

Chemical analyses by XRF, AA, Leco induction furnace for SO₃, and L.O.I. (loss on ignition) were obtained for the same size fractions (<45, <20, 14-5, 8-1 micron and the ball-milled 0-100 micron) used for the blends for the Series II paste mixes. These results show that our Vortec closed-circuit milling procedure, which retains the entire sample except for dust losses,

preserves the composition of the original clinker. There were, however, some small differences between the XRF and AA results for Al_2O_3 (AA was 0.1-0.2% higher) and between the original analysis and these results. Also, the narrower size fractions (14-5 and <20 microns) yielded higher results for alkalies by XRF for clinker 275; the AA results are believed to be more reliable. These results show that the particle size classified fractions have essentially the same compositions as the whole clinker; any differences in performance cannot be attributed to differences in composition.

3. Preparation of Cements

Each cement clinker was crushed, ground, and blended with ground gypsum to produce the cements. Normally ground clinkers were ball-milled to produced cements representative of normal commercial production. These had Blaine finenesses ranging from 3350 to 4100 cm^2/g and particle sizes ranging from about 100 microns to less than 1 micron. The particle size controlled cements prepared had Blaine finenesses ranging from 2106 to 3929 cm^2/g with maximum particle sizes ranging from about 44 to 14 microns and minimum sizes ranging from about 4.8 to 1.8 microns.

Since portland cements are normally interground with gypsum which grinds more easily than the cement clinker, the gypsum tends to concentrate in the fine fraction. Determination of the size distributions of the individual components (clinker and gypsum) in interground mixtures is difficult. Since in subsequent series we had to prepare known size distributions of the

ground cement clinkers, these were separately prepared and blended with the required gypsum. A total of 114 cements were prepared by blending ground clinker with gypsum as described below.

3.1 Gypsum Preparations

Terra Alba gypsum, available from the U.S. Gypsum Company, Southard, Oklahoma plant was used in five finenesses, one as supplied, and four finer grinds. This gypsum is recognized in ASTM C563 as suitable for determination of optimum SO_3 in portland cement. The material as supplied had a Blaine specific surface area (BSS) of $3533 \text{ cm}^2/\text{gm}$. Some of this material was ground in a small steel ball mill to finenesses of 5856, 7835, and $11448 \text{ cm}^2/\text{g}$. These four grinds are designated T.A.1,2,3, and 5 respectively. Table 4 gives the particle size distributions of these materials. The 90% size ranges are the sizes at the 95% and 5% levels of the cumulative mass percent distribution curves obtained with a Sedigraph 5000 Particle Size Analyser. T.A.4 was the T.A.2 material classified with a Vortec C-13 Particle Classifier to provide a fine fraction with particle sizes of less than 16 micron sizes. During the Series III preparations we somewhat fortuitously produced T.A.5 of $11448 \text{ cm}^2/\text{g}$ in attempting to duplicate T.A.3. This material was ball-milled to an apparent Blaine fineness of $7715 \text{ cm}^2/\text{g}$ (average for 2 batches). After V-blending the 2 batches the B.S.S. was $5400 \text{ cm}^2/\text{g}$; the material had apparently become badly agglomerated by exposure to humid air in the laboratory. After sieving to disperse agglomerates it had a measured Blaine fineness of $11448 \text{ cm}^2/\text{g}$.

3.2 Normally ground clinkers

The normally ground clinkers were ground in 2.5 to 4 kg batches in small (1 cu.ft) steel ball mills in a two step operation. The material was first ball-milled for 2000 revolutions in a mill containing 1.5 to 0.75 inch steel balls. This partially ground clinker was then transferred to a similar mill containing 0.87 to 0.5 inch steel balls and milled until the desired Blaine fineness was reached.

3.3 Particle Size Controlled Clinkers

To produce cements of controlled particle size distributions we developed a procedure of blending particle size fractions obtained from a Vortec Impact Mill and Classifier system. To understand how this is accomplished requires an understanding of the performance characteristics of the Vortec C-13 particle Classifier and the Vortec M-1 Impact Mill.

Performance characteristics of the Vortec M-1 Impact Mill are shown in Fig. 3. Cement clinker pulverized to minus 30 mesh was used as feed material, then passed repeatedly through the mill operating at 15,000 RPM to produce successively finer grinds. The most interesting feature of these curves is that the mill is capable of reducing the coarse fraction without excessive production of very fine (less than 2 micron) material as occurs in conventional ball-milling. This characteristic proves most useful when the mill and classifier are operated in closed-circuit so that the coarse material rejected by the classifier is returned to the mill for further grinding. This method of materials preparation has the advantage of using all of the feed material so that the composition remains unchanged.

If, instead, coarse and fine fractions are rejected, these may differ somewhat in composition leading to compositions that would vary with particle size range and complicate the interpretation of results.

The operating characteristics of the M-1 and C-13 operating in closed-circuit at various C-13 throttle settings are illustrated by the curves in Fig. 4. These curves are given for throttle settings that yield size fractions that begin at about 40, 20, and 12 microns at the coarse end. At the fine end the distributions do not terminate as sharply as desired. To achieve a more nearly linear distribution curve and a sharper cut-off it is apparent that additional material in the size range of the long tail of the curves (e.g. for MC 97 F additional material between 10 and 2 microns) is required. This is the basis for the method we have developed.

To test this method we classified the MC 10 F material in Fig. 4 in the Vortec C-13 at setting 5 at 5800 RPM. This yielded a coarse fraction with 90% between 13 and 4.3 microns and a fine fraction with 90% between 8 and 2 microns.

The amount of fine material to be blended with materials like MC 97 F and MC 25 F was determined by trial and error summations of the particle size distribution curves for different proportions of the fines with these materials. The results of such a trial calculation for the particle size distribution curve for a blend of 65% MC 97 F and 35% of the 8 - 2 micron fine fraction of MC 10 F are shown in Fig. 5. This blend closely approximates the desired curve shown by the

dashed line for the 45 - 2 micron range needed for the Series II tests. A similar curve for a blend for the 20-2 micron fraction is also shown.

For distributions that are to terminate at about 5 microns an additional classification step is required to remove the minus 10 micron particles in materials like MC 97 F and MC 25 F in Fig. 4. This step was necessary only for some of the rather artificial particle size distributions used in Series II.

3.4 Blending the Ground Clinker With Gypsum

In the early part of the program several methods of blending the gypsum with the cement were tried. These included use of a Kelly-Patterson V-blender, manual blending and sieving, and pebble milling. The effects of these variations are discussed in the next section along with the effects of gypsum fineness. Most of the cements were prepared by blending in a small ceramic mill with rounded flint pebbles. The mill was run with 1 to 1.5 kg of material and was nearly filled with pebbles so as to prevent any appreciable grinding action. This resulted in very uniform dispersion of the gypsum in the cement if the gypsum was first dispersed by passing through a 200 mesh sieve. This method was used for all but the Series I and a few other blends early in the work which are given in Table 5. Table 5 shows the 90% size ranges, the particle size distributions and the Blaine finenesses of these early blends; it also includes the cements prepared to test the pebble milling procedure. Table 6 contains the same kinds of data for the pebble milled blends, designated PM 1 to PM 87 used for most of the

work with the four clinkers used. A pebble milling time of 15 to 30 minutes was used for these cements.

4. The Effects of Gypsum Fineness

4.1 Series I Test Results

For the gypsum to be effective in control of the early hydration reactions of portland cement it must be ground finely enough to permit rapid dissolution in the mixing water. For commercial portland cements this is not normally a problem because the gypsum grinds more easily than the clinker as they are interground. This results in the gypsum concentrating in the finer size fractions in normally ground portland cements, as shown by the data of Swenson and Flint (Nat'l Bur. Standards Journal 17, 263, 1936). These authors separated 13 cements into the following size fractions, 0-7, 7-22, 22-40, 40-55 and >55-micron, and analyzed each fraction. A typical result for the SO_3 content of the different fractions is given in Table 7. Note that approximately 73% of the total SO_3 is found in the 0-7 micron fraction. This finely ground gypsum makes a substantial contribution to the Blaine fineness of the cements.

Since in the present work we needed to know the fineness and particle size distribution of the ground clinker itself we ground the components separately and blended them to make the cements. In the Series I tests we investigated the effect of variation of gypsum fineness to ascertain the fineness required in the following work. We used three different fineness, 3533, 5856, and 7835 cm^2/g . These Terra Alba gypsums are designated T.A. 1, 2, and 3 in Table 4. The high C_3A content clinker 275 was used for these Series I tests.

Because the setting times and strength development depends upon the gypsum content as well as fineness, blends of the ground clinker with gypsum were prepared ranging from 9.5 to 1.9 percent gypsum. These blends correspond to molar $\text{SO}_3/\text{Al}_2\text{O}_3$ ratios of 1.0, 0.8, 0.6, 0.4, and 0.2. Optimum gypsum content for normal setting behavior and maximum strength development was expected to be near the middle of this range. The 9.5% gypsum blend was prepared first as the primary blend, from which the lower gypsum contents were prepared as secondary blends with ground clinker. The primary blend was blended more thoroughly (1 hour in a V-blender) whereas the secondary blends were briefly dry-blended before mixing with water. These cements are designated V1 to V15 in Table 5. Visual examination of the primary blends revealed some agglomerates of the gypsum particles. However, these appeared to be dispersed during mixing with water, and there were no agglomerates or obvious inhomogeneities observed in the fracture surfaces of the specimens after compression testing, although some may have been present and lowered the strengths.

Batches of 200 grams of these blends were mixed with water at a water/cement ratio of 0.5 using a small electric mixer. Portions of each mix were used to cast 3 one-inch cubes in a stainless steel gang mold and to fill partially a 250 ml beaker for determination of the time of set using a modification of the standard Vicat needle method (ASTM C191). Time of set was determined as the time at which the penetration of a 2 mm Vicat needle was 10 mm or less. Cubes were cured at 73°F in a moist

closet for 1 day, 3 days, or 7 days. The cubes were then tested to failure in a compression testing machine. The results of these tests are given in Table 8. The strength data are also plotted in Figure 6 together with previous PCA data for gypsum interground (rather than blended) with this clinker to a fineness of the mixture of $3400 \text{ cm}^2/\text{g}$.

The results may be summarized as follows:

1. The setting times are independent of gypsum fineness and content from 3.8 to 7.6% gypsum. At the lowest gypsum contents the setting times are longer, indicating more rapid hydration of the aluminate phases, which delays the hydration of the silicates and normal setting. This is also shown the low 1-day strengths for the low SO_3 cements. Increasing gypsum fineness reduced this effect on setting time because the gypsum was more readily available to control the early aluminate hydration.
2. The strength data show relatively little scatter except for the as-is gypsum ($3530 \text{ cm}^2/\text{g}$) at the higher gypsum contents (5.7% and above). Since gypsum tends to pack and form agglomerates, this suggests lack of homogeneity and inadequate blending of the material.
3. Increasing gypsum fineness tends to increase strengths by about 20% at the highest gypsum contents but the effect is masked somewhat by the scatter of the 3 and 7 day results for the as-is gypsum.
4. Comparison of these Series I results with those previously obtained with interground gypsum shows that the strengths obtained are comparable over the middle of the range of

gypsum contents. The interground cements showed maximum strengths at about 5.5% gypsum, decreasing at higher gypsum contents as expected, whereas the blended gypsum cements increase or decrease less (this was not expected), especially for the finer gypsum cements.

Since these results were inconclusive, we conducted additional tests to investigate these effects. Although increasing gypsum fineness tends to increase strengths at higher gypsum contents the effect is small at lower gypsum contents. However, if the scatter of results was a result of agglomeration of gypsum particles some grinding of the as-is gypsum and/or more efficient blending was believed to be required. Since the gypsum requirements might also depend on the particle size distribution it seemed better to investigate the effects of blending techniques and gypsum fineness with particle size controlled cements, rather than repeating some of these mixes with the normally ground clinker.

4.2 Series II Preliminary Tests

The results of an additional test series called the Series II Preliminary tests are given in the next section (see Table 12). In these tests we used four particle sized controlled and one normally ground clinker with T.A.2 of $5856 \text{ cm}^2/\text{g}$. These cements are designated MB1 to MB5 in Table 5. Results are given in Table 9 for the mini-slump pat areas used to measure paste flow properties.

These results suggested that the flow may be strongly affected by how the gypsum is blended with the ground clinker.

A single result for this cement with interground gypsum yielded a much larger slump as shown in Fig. 7.

4.3 Additional Tests of Paste Flow Properties

Such results indicated a need to improve the blending of the gypsum with the ground clinker. In Series I the gypsum was V-blended with the ground clinker but gypsum agglomerates were not completely dispersed; visible specks remained which may have affected the results. These visible specks were eliminated in the Series II Preliminary Tests by 200 mesh sieving the 5856 cm²/g gypsum before blending manually. Since the minislump values, bleeding, time of set, and strength all depend on early reaction control, which depends on gypsum fineness and dispersion, and the bleeding depends directly on gypsum fineness, we repeated the Series II Preliminary Tests with a finer gypsum to determine the effect on the minislump values. This finer gypsum was obtained by classifying the 5856 cm²/g material in the Vortec C-13 Particle Classifier to remove the +15 micron particles. This yielded a fine fraction designated T.A.4 of 7573 cm²/g Blaine, which was manually blended with the same four size fractions of clinker 275, sieved (200 mesh) to disperse agglomerates, and mixed at 0.5 water/cement ratio for mini-slump tests. These cements are designated MB6 to MB9 in Table 5. The results of these tests are compared in Table 9 with those previously obtained with the 5856 cm²/g gypsum.

Since the pat areas are all smaller for the higher Blaine gypsum it appears that good early reaction control was achieved in both cases; the lower values are mainly a result of the physical effect of the finer gypsum. The results agree well

with those obtained earlier when plotted versus water film thickness (Fig. 7).

To develop a method of blending in the gypsum that was better than V-blending or manual blending, we decided to examine the effects of pebble milling for various short time periods. The objective was to produce good dispersion, to control early reactions and to obtain consistent values for the mini-slump, without appreciably changing the original particle size distribution or Blaine fineness. Two series of tests were made both using the 14-5 micron fraction of clinker 275 of 2114 cm^2/g Blaine. In the first we used the 5856 cm^2/g Terra Alba gypsum (not sieved) in cements designated V16 and PMT1 in Table 5. In the second we used the ball milled T.A.3 7835 cm^2/g gypsum (also not sieved) in cements designated V17 and PMT2 in Table 5. We had hoped that the pebble milling would disperse the gypsum agglomerates after some relatively short time, but this was not the case. Some visible specks remained after even 1 hour of pebble milling. In the first series a charge of 3,100 g of cement was used with 1,550 g of flint pebbles. In the second, a charge of 1,500 g of cement was used with 1,500 g of pebbles in hopes of more effective dispersion of the gypsum agglomerates. In both cases the cement was blended in the V-blender for 15 minutes before pebble milling, as was done in Series I. The results of the Blaine measurements and mini-slump tests are shown in Table 10.

These results show:

1. the Blaine value increases very slowly with the pebble milling time, about 35 $\text{cm}^2/\text{g}/\text{hour}$ in the first case.

In the second case a plot of the B.S.S. versus time shows a more rapid increase in the first 15 min., then remaining nearly constant for 1 hour, averaging 77 $\text{cm}^2/\text{g}/\text{hour}$.

2. the initial mini-slump pat areas for the two gypsum finenesses agreed very well; both decreased slightly during the first 15 min. of pebble milling, but remained constant thereafter.
3. The average pat areas (5.87 in.^2 and 5.86 in.^2) for the two gypsum finenesses agreed. Variations in each series indicate more scatter than significant effect of milling time after 15 min.

It therefore appeared that pebble milling for 15 minutes would have no significant effect on the Blaine finenesses and would yield reproducible minislump pat areas. As noted earlier, visible gypsum specks (agglomerates) were not seen in blends in which the gypsum had been sieved before blending. Hence it was decided that in all future blends the gypsum would be sieved first, and the cements would be pebble milled for 15 to 30 minutes.

4.4. The Effect of Gypsum Fineness on Strength

There remained, however, questions concerning the effect of gypsum fineness on strength and what fineness to use in the tests to follow. We suspected that none of the four gypsum finenesses that had been used were fine enough to have the effect of interground gypsum. The Series I results in Table 8 and Fig. 6 showed a clear optimum gypsum maximum only at one day and this was at 7.6% gypsum, significantly higher than the

value of 5.5% found for the interground gypsum with this clinker. For the Series II work we decided to use the finest gypsum we had ground, T.A.3 of $7835 \text{ cm}^2/\text{g}$. During the Series III work we somewhat fortuitously produced T.A.5 of $11448 \text{ cm}^2/\text{g}$ in attempting to duplicate T.A.3. See section 3.1. After ball-milling, this material had a Blaine fineness of $7715 \text{ cm}^2/\text{g}$ which increased after sieving to a fineness of $11448 \text{ cm}^2/\text{g}$. At the time it was thought that this must also have been the case for T.A.2 and 3. The BSS values given for these grinds were the values obtained after milling; they were not sieved initially. The matter was investigated thoroughly when the Series III cements were prepared because the Blaine finenesses of the pebble mill blends turned out to be much higher than anticipated; this was a result of the high fineness of T.A.5. We then calculated the apparent BSS values of the gypsum in the Series III pebble-milled blends from the BSS values of the PM blend and that of the ground clinker fraction. These calculated values yielded an average of about $12700 \text{ cm}^2/\text{g}$, slightly higher than that for the sieved gypsum. Similar calculations for the Series II PM blends using T.A.3 also yielded a value for the apparent fineness of the gypsum in the blend, $8500 \text{ cm}^2/\text{g}$, only slightly higher than the measured values for TA3, $7835 \text{ cm}^2/\text{g}$. Hence we concluded that T.A.2 and 3 had not been so badly agglomerated as T.A.5 was after milling and that their B.S.S. values were approximately correct.

With the finenesses of the gypsums in the PM blends established with confidence we can now reexamine the effect of gypsum fineness on strength development. In Table 11 we have collected

pertinent ball-milled clinker data from Series I, II, and III for comparison with a set of data previously obtained with clinker 275 interground with gypsum to obtain cement with a Blaine fineness of $3400 \text{ cm}^2/\text{g}$. These data show that the one and seven day strengths increased with increasing gypsum fineness and amount (up to 7.6%) until we reached the $11448 \text{ cm}^2/\text{g}$ gypsum. These Series III paste strengths more closely resembled the behavior of the interground gypsum pastes; both showed lower 1 and 7 day strengths at 7.6% gypsum than at 5.7% gypsum. The values are somewhat different because of differences in the finenesses of the ground clinker and cements. Also, the Sedi-graph curve to T.A.5 showed that 73% was finer than 17 microns, somewhat coarser than indicated by the data of Swenson and Flint for interground gypsum.

4.5 Fineness Determinations - Which are Correct?

Although it may appear that we have labored the point somewhat it is important to recognize that in normally interground cements the gypsum makes a substantial contribution to the Blaine fineness. In consideration of the energy conservation potential of variations in fineness of grinding we must compare with cements as they are now normally ground. The data in Table 11 indicate that the Blaine fineness of the gypsum in interground cements is very high (at least $12000 \text{ cm}^2/\text{g}$) and that the fineness of the clinker fraction is correspondingly lower. Calculated values for the Blaine finenesses of the clinker in these interground mixtures are given in the table.

For many years there has been some confusion on these points partly because of uncertainties in the methods of measurement

of the specific surface areas of cements. Two methods have been in common use since the 1930's: the Blaine air permeability method, and the Wagner turbidimeter method. The Blaine values are commonly about 1.8 times the Wagner values. The Wagner method determines the particle size distribution from about 45 microns to 7.5 microns; the specific surface is calculated from this curve using an extrapolation procedure for the less than 7.5 micron fraction. Since most of the specific surface is in the less than 7.5 micron fraction the result depends heavily on the extrapolation procedure. We have long felt that the Wagner method grossly underestimates the true specific surface areas. Some researchers have felt that the Wagner method gave a better estimate of the true surface area because those values correlated better with 28-day strengths than the Blaine values and that there was some serious error in the Blaine method. The results obtained in this study indicate that the Blaine values are more nearly correct and agree quite well with values calculated from the Sedigraph particle size distribution curves. The Sedigraph curves yield the entire size distribution down to a fraction of a micron and do not depend on an extrapolation procedure. Hence some of the early work such as that of Swenson and Flint cited earlier was somewhat misleading in their estimates of the contributions of the gypsum to the specific surface, because they used Wagner values for the specific surface which are only about 56% of the Blaine values. The present work should help to eliminate the confusion which has so long existed on these points.

4.6 Future Considerations

In the sections to follow we will be concerned mainly with variations in the particle size distributions of the ground clinker in the cements. It will be shown in the Series III results that even when very finely ground gypsum is used, the gypsum requirements, or the amount of gypsum which can be advantageously used, are higher than the optimum gypsum for normally ground cements. This enables us to utilize the clinker more fully for strength development, and also, has favorable implications with respect to the use of cements made from high sulfur fuels.

5. Effects of Large Variations of Particle Size Range and Gypsum Content on Fresh Paste Properties and Strength Development

5.1 Series II Preliminary Tests

Before preparing the substantial quantities required for the Series II tests the preliminary grinds of clinker 275 were used for a series of test mixes to reveal any unanticipated difficulties in mixing and casting specimens. Four controlled particle size ranges designated MB1-MB4 in Table 5 were used yielding the results given in Table 12. These ground clinker fractions were manually blended with T.A.2 gypsum ($5860 \text{ cm}^2/\text{g}$ Blaine) to yield cements of 5.7% gypsum ($\bar{S}/A = 0.6$). Results obtained in Series I for the ball-milled clinker (normal particle size distribution) of $3600 \text{ cm}^2/\text{g}$ are also shown for comparisons. These results show that:

1. All of these particle size distributions yielded workable mixes as indicated by the mini-slump pat areas.

Paste consistencies varied considerably with variations at the fine end (2-5 microns) but were relatively insensitive to variations at the coarse end (14-45 microns). Fig. 7 shows the relationship between the mini-slump pat areas and the average water-film thickness calculated from the Blaine specific surface and water-cement ratio. This is nearly linear and indicates zero slump (pat area = 1.77 in.^2) at a water film thickness of about 1.1 micron. Figure 8 shows the pat area as a function of the percentage of minus 5 micron material. This indicates zero slump at 44% finer than 5 microns. However, at lower Blaine fineness, corresponding to water-film thicknesses greater than 2 microns, the pat area increases rapidly even with 8% finer than 5 microns. These plots indicate that the slump is directly related to the Blaine surface or water film thickness but may also be related to the size range.

2. The small amount of bleeding from the 45-2 and 20-2 micron fractions is normal, or even less than the normal range as given by Steinour (p. 23, PCA Bull. 4). The 45-5 and 14-5 micron materials, however, showed excessive bleeding, this being about 19 percent of the paste volume. This corresponds to a reduction of the original water cement ratio of 0.5 to about 0.35. Since even the 14-5 micron fraction showed about the same bleeding as the 45-5 micron fraction, the 2-5

micron fraction appears to have the greatest effect on bleeding control at this water-cement ratio.

3. All mixes yielded normal setting times.
4. As expected, the 45-2 and 20-2 micron fractions show exceptionally good strength development. Strength development of the 45-5 and 14-5 micron fractions was poor considering their low actual water-cement ratio (0.35).

These preliminary results were encouraging in that they indicated that our original estimate of the desired minimum size had been properly bracketed between 2 and 5 microns. The +5 micron material bleeds excessively whereas the +2 micron material does not, shows very good strength development, but tends to produce stiff mixes.

5.2 Series II Tests

Two cement clinkers were selected for the Series II tests, the high- C_3A clinker 275, with a calculated C_3A content of 12.11%, and the low C_3A clinker 274 with a calculated C_3A content of 6.85%. In both cases, the desired particle size distributions were obtained by blending several primary size fractions produced in the Vortec Mill-Classifier System as described in Section 2. Ball-milled clinker cements were used as controls, nominal size range 100-0 microns.

The cements were prepared as pebble mill blends of the primary clinker size fractions with added Terra Alba (T.A.3) gypsum of 7835 cm^2/g Blaine fineness to yield cements with molar sulfate to aluminate ratios ($\bar{S}/A$) of 0.4, 0.6, and 0.8. The percentages of the primary clinker size fractions used and other

data for these pebble milled blends (PM 1 to PM 30) are given in Tables 13 and 14. As expected, the Blaine specific surface and the L.O.I. both increase with the gypsum contents. The particle size distribution data are given in Table 6. The particle size distributions of the 274 cements agree well with the corresponding blends of the 275 cements except for the ball-milled controls; clinker blend PM 29, has a somewhat lower B.S.S. (3655 cm²/g) than that of the ball-milled cement PM 14 (4022 cm²/g). This difference should not complicate interpretations of the data for each clinker; Blaine values for the different size ranges vary much more than this.

Clinker 275

The results of measurements on paste mixes at water-cement ratios of 0.35, 0.50, and 0.65 are given in Table 15 for the 275 cements.

Workability. The mini-slump pat area data for the 5.7% gypsum blends are also shown in Fig. 9. No points were obtained at 0.35 water-cement ratio because these mixes were too stiff to slump. However, prior work by Dr. Kantro, in this laboratory, has shown that such plots are nearly linear over a range of water-cement ratios, so that the two points at 0.5 and 0.65 were used to determine the straight line relationships. For the 45-5, 14-5, and 100-0 micron cements, these are parallel lines, the 45-5 micron being above and the 14-5 micron being below the controls (100-0 microns). The 45-2 and 20-2 micron cement lines are lower (less workable) and have lower slopes (less sensitive to water/cement ratio). These are not workable below 0.5 water/cement ratio although the Blaines were not excessive. They have even more 2-5 micron material than the controls.

Figure 10 shows the same data for all three gypsum contents plotted against the average water-film thickness calculated from the water-cement ratio and Blaine Specific Surface of the cement. These plots have about the same slopes, but are displaced from each other. In terms of the water-film thickness the 100-0 micron ball-milled material has much better workability at higher ($4000 \text{ cm}^2/\text{g}$) Blaine values than any of the narrower size ranges. Hence, the Blaine (or water-film thickness) is not the only factor; gradation is also important.

Bleeding. Excessive bleeding was shown by some of the pastes at the higher water-cement ratios. The amount of bleeding is indicated by the water-cement ratios corrected for bleeding given in Table 15. The 45-5 micron cement showed the greatest bleeding, the 14-5 micron cement the next highest, but at 5.7% gypsum ($\bar{S}/A = 0.6$), not much worse than the controls, which also bled excessively at high water-cement ratio.

The 45-2 and 20-2 micron cements bled very little, the 45-2 micron cement showing more, but less than the controls except at $\bar{S}/A = 0.6$ (5.7% gypsum) where it is about the same as that of the controls.

Setting Time. Nearly all pastes set approximately normally, the 45-5 and 14-5 micron cements a little more slowly than the controls, the 20-2 and 45-2 micron cements a little faster than the controls. One low water content mix was so stiff it was "set" upon mixing.

Strength. Particle size control produced extremely wide variations in compressive strengths and rate of strength development at all water-cement ratios. Since the bleeding

caused wide variations in water-cement ratios, the water-cement ratio used in the following are those corrected for bleeding so that valid comparisons can be made.

The major effects on strength of the 2-5 micron clinker particles are shown in Figs. 11 and 12 for the 7.6% gypsum cements. In Fig. 11, the 45-2 micron particle size cement ($3679 \text{ cm}^2/\text{g}$), is compared with the 45-5 micron cement ($2409 \text{ cm}^2/\text{g}$). Also shown is the data for the 100-0 micron ball-milled cement ($4108 \text{ cm}^2/\text{g}$) used as a control. At one day the strengths of the 45-5 micron cements are very low whereas the 45-2 micron cement strengths are even better than the controls, despite the fact that the Blaine fineness is lower. The differences are not as great after 28 days, but the 45-2 micron cement strengths are still higher, especially at higher water-cement ratios.

Similar differences are seen in Fig. 12 for the 20-2 and 14-5 micron size ranges. At one day the strength differences are very large and again, despite the fact that the Blaine fineness is lower, the strengths of the 20-2 micron cement are much greater than the controls. However, at 28 days the 20-2 micron range does not develop as good strengths as the 14-5 micron size range at low water-cement ratios. This is consistent with our simple model of paste structure which indicates that an excess of fine particles with relatively thick water-films limits the ultimate strength. However, of perhaps greater importance is the much greater decrease in strength with increasing water-cement ratio shown by the 14-5 micron cement. The 20-2 micron cement is much less sensitive to increasing water-cement ratios.

The effect of reduction of the maximum size from 45 to 20 or 14 microns is shown by comparing the results in Fig. 11 with those in Fig. 12. As expected, the smaller maximum sizes do produce somewhat better strength development. For the 45-5 and 14-5 micron size ranges the effect is appreciable only at the lower water-cement ratios. For the 45-2 and 20-2 micron size ranges, the effect is appreciable only at high water-cement ratios at early ages (at both 1 and 7 days).

Results at 5.7% gypsum ($\bar{S}/A = 0.6$) were similar to those at 7.6% gypsum, except that the strength of the 20-2 micron size range at 28 days at low water-cement ratio is even lower than at 7.6% gypsum; this is thought to be due to an excess of fine particles. At 3.8% gypsum the 1 day strengths were low.

Clinker 274

The results of measurements on paste mixes of the clinker 274 cements are given in Table 16.

Workability. The mini-slump pat area data qualitatively similar to those obtained with the high C_3A clinker 275. The sequence of variation of the pat areas with the size ranges is the same as in Fig. 9. The flow, however, is appreciably greater for the low C_3A clinker than for the high C_3A clinker. It was possible to obtain mini-slump data at 0.35 water-cement ratio with those cements, whereas with clinker 275 it was not. The water requirement for the clinker 274 cements for the same flow as the clinker 275 blends is from 11 to 17% less than for clinker 275 at 0.65 water-cement ratio.

This difference in water requirement is believed to be a result of differences in the early hydration reactions of the

aluminates. The cements were made at equal sulfate to aluminate ratios; hence the high C_3A cements had higher gypsum contents than the low C_3A cements. However, these differences in flow are much greater than can be accounted for in terms of gypsum content, per se; the plots in Fig. 10 show only small variations of flow with gypsum content. Hence, the differences between the high and low C_3A cements are not merely a physical effect of the finely ground gypsum, but appear to depend upon the differences in C_3A contents of these clinkers, and their early hydration reactions.

Bleeding. The bleeding water loss indicated by the corrected water-cement ratios show that these pastes bled slightly more than did the corresponding mixes made with the high C_3A clinker. The 45-5 and 14-5 micron particle size ranges showed excessive bleeding, much greater than the controls (100-0 microns).

Setting Time. All of the pastes had normal setting times. The 20-2 micron particle size cement showed the most rapid setting. There was less variation with particle size range and gypsum content than with the high C_3A cements.

Strength. The variations in compressive strengths with particle size range, water-cement ratio, and curing time are similar to those found with the high C_3A clinker 275. These cements usually yielded lower strengths than the high C_3A cements for comparable mixes. The degree of hydration of the low C_3A cement may be lower at equal ages, which may partly account for the differences. (See Series III data).

The 45-2 micron cements yielded strengths very little different from the controls (100-0 microns) at the two higher gypsum contents. The 45-5 micron cements yielded much lower strengths, as was also the case with the high C_3A cements. The 20-2 micron cements showed even better strength development relative to the controls than the clinker 275 cements, especially at 1 day, and at later ages at all water-cement ratios. In contrast with the 28 day results for the high C_3A cements, these 20-2 micron cements developed better strengths than the 14-5 micron cements at low water-cement ratios as well as at high water/cement ratio.

The most significant difference between the 20-2 and 14-5 micron size ranges is in the amounts of 2-5 micron size particles, which are 27% and 5%, respectively; the controls have about 13% in this size range. (See Table 6).

For the 45-5 and 14-5 micron cements the effect of reduction of the maximum particle size on strength was appreciable only at the lowest water-cement ratio, which is similar to the results with the high C_3A cements. For the 45-2 and 20-2 micron cements the increase in strength is much greater than found for the high C_3A cements, being appreciable at all ages and water-cement ratios.

The data given in Table 16 for these low C_3A cements with 3.78% gypsum also show the effect of reducing the maximum particle size from 45 to 20 microns. The strength data show that at 7 days the strengths of the 20-2 micron cement are even higher than the 28 day strengths of the controls and the 45-2 micron

cements at most water-cement ratios. The 45-2 micron cement contains almost as much (21%) of the 2-5 micron material as the 20-2 micron cement (27%). Hence, the improved strengths seem to be mainly a result of the reduced maximum size. Since similar benefits were not obtained when only little 2-5 micron material was present, an appreciable amount of 2-5 microns seems necessary to obtain increased strengths at reduced maximum particle sizes, except at low water-cement ratios.

5.3. Discussion of the Series II Results

In the proposal for this work the importance of the 2-5 micron particle size range and the upper limit on particle size were recognized and have been amply confirmed by these Series II results. The flow and bleeding properties of the fresh pastes and the early strengths are very sensitive to the amount of 2-5 micron material. With little 2-5 micron material the flow was improved, but the bleeding was excessive, and the strengths at early ages and at later ages at the higher water-cement ratios were poor. Such cements obviously require more 2-5 micron material. On the other hand, the paste flow properties of cements with 21-26% of 2-5 micron material were poor, and in some cases failed to reach strengths expected at low water-cement ratios. Such cements apparently contain too much 2-5 micron material.

The fresh paste properties are not very sensitive to the upper size limit. The increase of the strengths with reduced maximum particle size appears to depend on the C_3A content, age, water-cement ratio, and the amount of 2-5 micron material.

The particle size requirements for good flow conflict with the requirements for good strength development. If strength were the only requirement cements close to the 20-2 micron size range would be superior for their high strengths, especially at early ages, and also for their low bleeding capacity. The strengths of 3-4 ksi (at w/c of 0.45) obtained at 1 day for these cements are outstanding, considering the fact that the Blaine finenesses were no higher than those of the controls. However, the high water requirement for flow of these 20-2 micron cements is difficult to understand in terms of the average water-film thickness calculated from the Blaine specific surface and water-cement ratio. A better understanding of the effect of the particle size distribution on the flow properties would be desirable in order to achieve a rational compromise between the requirements for acceptable flow and good strength development.

5.4 Analysis of the Water Requirement for Flow

It has been assumed that if the average water-film thickness, t , were properly calculated there would be a single systematic relationship between the flow (mini-slump pat areas) and t for the different particle size distributions. Such a relationship was in fact indicated by the Series II Preliminary Test results presented in Fig. 7. The more complete data in Fig. 10 show that this is not the case for t calculated by dividing the water-cement ratio by the B.S.S. However, these plots are more systematic in some ways than the plots against w/c as in Fig. 9. For example, the data in Fig. 10 for the 45-5 micron cement and the 20-2 micron cement lie on nearly the

same straight lines. Also, the plots shift systematically with increasing ratios of the maximum to minimum sized particles. Such systematic shifts suggested that there may be some systematic error in the calculation of t , either in the value of the B.S.S. or the value of the water content which is effective for flow in the fresh pastes after mixing.

Several factors were considered and trial calculations made of corrected water-film thicknesses in attempts to obtain a single relationship between the flow and calculated film thickness.

1) One factor that was considered was that the smallest particles, below some minimum size, may dissolve completely in a few minutes after mixing. To obtain a B.S.S. value corrected for this effect, the contribution of the -2 micron particles to the B.S.S. was calculated from the Sedigraph curves and subtracted from the B.S.S. This reduced B.S.S. was used to calculate the water-film thickness corrected for this effect. The results of such calculations yielded plots for the different particle size ranges that were in better agreement than those in Fig. 10. Calculations were also made using minimum sizes of 1 micron and 4 microns, but the best agreement was obtained at 2 microns.

Encouraged by this improvement more detailed calculations were made.

2) In a second calculation several factors that may affect the calculated water-film thickness were considered. For this calculation two reasonable assumptions were made concerning the immediate hydration reactions: (1) gypsum particles dissolved

at equal rates from their outer surfaces, and (2) gypsum control was rapidly attained by formation of ettringite coatings on the C_3A surfaces at 10% of the C_3A reacted. The fraction of the gypsum dissolved was then calculated for the 3.8, 5.7 and 7.6% gypsum contents of the 275 cements. The depth of dissolution of the gypsum particles was then calculated from the gypsum particles size distribution curve for the fraction dissolved. From the depth of dissolution, the particle size distribution and the B.S.S. of the undissolved gypsum was then calculated. Then the reduction of the B.S.S. of the cements due to dissolution of the gypsum was calculated. These results were as follows:

% gypsum	3.8	5.7	7.6
% of the gypsum dissolved	62.9	41.9	30.1
Depth of dissolution of gypsum particles (microns)	1.1	0.45	0.28
B.S.S. (cm^2/g) of undissolved gypsum	2030	3150	4024
Reduction of B.S.S. of cement due to gypsum dissolution	268	342	382

Also considered was the effect of the ettringite coatings on the C_3A surfaces on the B.S.S. of the cement. From the Blaine fineness of the various particle size cements the depth of reaction required for 10% reaction of the C_3A was calculated to be only about 0.1 microns. This was considered to be too small to have an appreciable effect on the B.S.S. of the cement and was neglected.

One additional factor considered was the reduction of the free water content by the hydration of 10% of the C_3A to form ettringite. This was calculated to be 0.021 g/gc so that the

original water-cement ratios of 0.65, 0.50, and 0.35 were reduced to 0.629, 0.479, and 0.329, respectively.

When these corrections were made for the reduction of the B.S.S. due to gypsum dissolution and the reduction of the free water content the plots of the pat areas vs the corrected water-film thickness were very little different from the uncorrected results plotted in Fig. 10.

3) In the above, the dissolution of only the gypsum particles was considered to reduce the Blaine fineness of the cements. If, in addition to the above corrections all of the particles of cement clinker finer than 2 microns are considered to dissolve, the agreement between the pat area vs corrected water-film thickness plots for the different particle size range cements is again improved. However, it now appears that such improved agreement may have been fortuitous because the water content that should be used to calculate the water-film thickness may be much less than the actual water content.

4) The pat area vs water/cement ratio plots of Fig. 9 suggest that the effective water content for flow is much less than the total water content of the paste. The linear plots extrapolate from the high water/cement ratio points to minimum pat areas (zero flow) at water/cement ratios ranging from 0.34 to about 0.46. A considerable amount of water is required before any flow can occur. Water trapped in the interstices between the particles will not contribute to increasing the water-film thickness or the interparticle spacings. Also, interparticle forces cause the formation of floc structures in which water

may be trapped without contributing to the paste flow. Evidence for such effects was obtained many years ago by Powers and Steinour in their studies of bleeding (PCA Res. Dept. Bulletin 2,3, and 4). Recently Rendchen (Beton. Herstellung. Verwend. 26 (9), pp. 321-325, 1976) found that the dynamic viscosity of portland cement pastes could be represented as a simple function of an interparticle spacing calculated from the water content, w , (the water/cement ratio) and an inactive water content, w_a , as:

$$\frac{(w - w_a)^2}{B.S.S.} \times 10^4 \quad (\text{in microns})$$

Rendchen found empirically that values of w_a of about 0.3 yielded best fits for the flow data.

5.5 Direct Measurement of the Inactive Water

In an attempt to obtain an independent measure of the amount of the interstitial or inactive water, which includes the hydrate water formed in the initial reactions, a short series of tests were performed. In these tests pastes of each of the particle size ranges of the clinker 275 cements were mixed at a water-cement ratio of 0.5 and compacted in a Carver press at moderate pressure (500 - 2,500 psi) to remove the excess water. These pressures should be sufficient to bring the cement particles into contact with negligibly thin water-films between them. Then the remaining water should be essentially the interstitial and hydrate water, and the amount of this water should depend upon the particle size gradation. A wide particle size range should have less pore volume than a narrow particle size range.

The amount of water retained decreased slightly with increased compaction pressure. Plots of water retained vs compaction pressure were extrapolated to zero compaction pressure to obtain values of w_a/c appropriate for the fresh pastes as mixed. These values of w_a/c were then subtracted from the water-cement ratios to obtain the water which contributes to inter-particle spacing. Several trial calculations were made using the original B.S.S. values and B.S.S. values corrected for effects previously discussed. None of these calculations yielded a single flow vs water-film thickness relationship that applied to all of the particle size ranges. However, the data did show that the amount of water retained by the narrower size range cements is considerably greater (about 0.32 to 0.38 g/gc) than that found for the normal grind cement (0.25 g/gc). This difference is in qualitative agreement with the better flow characteristics of the normal grind cement at equal calculated average water-film thicknesses shown in Fig. 10.

5.6 The Need for Additional Tests

The wide variations in flow properties seen in Series II are much greater than anticipated for cements that have B.S.S. values no higher than the controls. These variations are due mainly to the large differences in the amounts of 2-5 micron particles (5% vs 20-25%). Since these differences were so large, and the paste properties were so sensitive to these amounts, it was difficult to decide on the intermediate amounts required for the Series III tests. If the blend proportions had been incorrectly selected much of the data would have been useless.

6. Effects of Particle Size Ranges on Strength and

Drying Shrinkage

6.1 Series III Preliminary Tests

The wide variations in paste properties found with the Series II cements made it difficult to make reasonable estimates of the amounts of fines required for the cements to be used in the Series III tests. Hence, a short series of preliminary tests was made to more narrowly define the amounts of fines requires to obtain both adequate flow and strength development. These cements were prepared from excess materials remaining from the Series II preparations. The proportions of the primary size fractions for these blends were chosen to provide intermediate amounts of fines in blends otherwise similar to those used in the Series II tests. Primary particle size fractions of the low C_3A cement clinker 274 with maximum particle sizes of 45, 20, and 14 microns were blended with various amounts of the 8 to 1 micron fraction and 3.78% gypsum to produce these cements. The proportions used are given in Table 17. Blaine finenesses are also given.

The size ranges used in Series II were obtained by blend proportions that terminated rather sharply at each end. Hence, they were designated 45-2, 20-2 etc. microns. In the present series the termination of the fine end is not so sharp and the size ranges are designated 45-X, 45-Y etc. to reflect this fact. The actual particle size distribution curves are given in Table 6.

Procedures used were the same as used in the Series II tests for materials preparation, mixing, mini-slump cone flow tests,

and setting time. However, for this test series only, 1x2-inch cylinders were cast for strength tests instead of 1-inch cubes as otherwise used.

The results of these tests are given in Table 18. The strength data are given as strengths for 1-inch cubes calculated from the cylinder strengths for comparison with the Series II data. Since the ratio of cylinder strengths to cube strengths is about 0.8 (F.M. Lea, The Chemistry of Cement and Concrete, 3rd Edition, Chemical Publishing Company, 1971, p. 390), this factor was used to obtain the calculated cube strengths. This factor appears to yield reasonable strength relationships between these and the Series II test data.

Some of the data are plotted in Figs. 13 and 14. Fig. 13 gives the mini-slump pat areas for the 45 and 20 micron maximum size cements and includes the Series II results for the controls (100-0 microns, ball-milled) and for the 45-2 and 20-2 micron particle size cements at 3.78% gypsum. These plots show the expected progressive increase in water requirement for flow with increasing content of added fines. To provide some basis for comparison it should be noted that previous work (on another project) has shown that to obtain workable concrete (2 to 3-inch slump) with normally ground cements at water-cement ratios of 0.41 to 0.43 the pastes should have pat areas of at least 5 in.² This requirement was met by the pastes made with the normally ground cement, but some of the other pastes had smaller pat areas and may not yield workable concretes (see later for further discussion).

The bleeding data also show the expected progressive decrease in bleeding with increasing content of added fines.

The compressive strength data for the less than 20 micron particle size cements and the ball-milled controls are shown in Fig. 14 for the values at 1 and 28 days as functions of the water-cement ratio corrected for bleeding.

Since our major concern here is the amount of fine material required to reach satisfactory compromise between the flow and strength development these properties will be discussed together for each size range.

1. Figure 13 shows that for the cements with 45 micron maximum size particles the addition of 8 to 1 micron fines to the 45 micron primary size fraction results in progressively higher water requirements for flow. With 10 and 15% of added fines the flow was greater than that of the controls; at 25 and 35% of added fines the flow was less than that of the controls. The 1 and 28 day strengths exceed those of the controls only when the added fines exceed 25%. Even when 35% of added fines are used, the strengths are only slightly higher than those of the controls. This blend may yield workable concretes with this low C_3A content cement, but at 35% added fines the strengths are only slightly better than with 25% fines and the B.S.S. ($3316 \text{ cm}^2/\text{g}$) is approaching that of the control cement ($3655 \text{ cm}^2/\text{g}$).
2. Similar tendencies were shown for the cements with 14 micron maximum sized particles with additions of the 8

to 1 micron fines to the 14 to 5 micron primary size fraction. In this case the B.S.S. values are all considerably less than that of the control cement. With 0% added fines the water requirement for flow is about the same as that of the controls; addition of up to 25% fines caused a progressive reduction of the flow. The strengths of the 0% and 10% added fines cements were less than the controls. At 25% added fines the strengths slightly exceeded those of the controls, as in the case of the less than 45 micron cements. However, these improved strengths were achieved at a lower B.S.S. ($2930 \text{ cm}^2/\text{g}$) than with the less than 45 micron cements. In both cases the gains in strengths are achieved with some loss of flow.

3. The case of the 20 micron maximum particle size cement is interesting because the strengths, shown in Fig. 14, are significantly greater than those of the strongest less than 14 micron cement at about the same B.S.S. ($2970 \text{ cm}^2/\text{g}$ with 15% added fines) while the flow values are also slightly better. The bleeding was also less. Hence, some strength could be sacrificed to achieve better flow by some further reduction in the amount of added fines, to perhaps 10%, with some further reduction of the Blaine fineness. Even with 15% added fines the Blaine fineness is significantly less than that of the control cement ($3655 \text{ cm}^2/\text{g}$).

Since the strengths were increased by increasing the maximum size from 14 to 20 microns (at the same B.S.S.) it also

seemed possible that some further increase could be achieved by increasing the maximum size to perhaps 30 microns. At 45 microns the strengths are again lower. Increasing the maximum particle size should also improve the paste flow as seen by the comparison of the less than 20 and less than 45 micron cements in Fig. 13.

However, another factor to be considered concerning the effect of the maximum cement particle size on the flow is that in concretes the largest cement particles interfere with the flow of fine aggregate particles. This is discussed in Powers' book (Ref. 25, the proposal for this work) where it is noted that lower water-cement ratios can be used with finer cements in concretes although the paste itself may be of stiffer consistency. Hence it seemed that it might be possible to use a cement like the 20-Y cement with even more than 15% of added fines at as low water-cement ratios in concrete as is possible with the control cement. Series IIIa provided an opportunity to test for this effect.

The results of these tests more narrowly defined the particle size distributions required for the Series III tests. The data showed that a maximum particle size of 20 microns is better than 14 microns, and that it might also be advantageous to increase this to 30 microns, which would also be easier to achieve in practice. These data also showed that the amounts of fines to be added for optimum performance seem to lie between about 10 and 25%, depending on how sensitive the workability of the concrete is to variations of the maximum size of the cement particles.

6.2 Series IIIa - Preliminary Concrete Tests

The Series IIIa work was planned to determine whether there might be any unanticipated problems with use of the particle size controlled cements when used in concretes. A very limited series was performed that did not require large quantities of cements. Hence, there was not much opportunity to use trial mixes to obtain the optimum proportions to be used.

Two particle size controlled cements were prepared from the low C_3A content clinker 274, PM 64 with 30 micron and PM 65 with 20 micron maximum sized particles, each with 15 percent added clinker fines. The normally ground cement PM 43, used as a control, had a Blaine fineness of $3661 \text{ cm}^2/\text{g}$; PM 64 and 65 had Blaine finenesses of 3160 and $3600 \text{ cm}^2/\text{g}$, respectively. Complete data are given in Tables 6 and 19.

Because of our concern that the water requirements of PM 64 and 65 might be excessive, we first made mortars with these cements and determined the mortar flow by the ASTM C109 procedure. These tests yielded the following results:

<u>Cement</u>	<u>B.S.S.*</u> <u>cm^2/g</u>	<u>Mortar</u> <u>Flow</u>
PM 43 (ball-milled)	3661	101
PM 64 (30 microns maximum)	3160	114
PM 65 (20 microns maximum)	3600	109

*Blaine Specific Surface Area

These tests showed that both of the controlled particle size cements (PM 64 and 65) yielded better mortar flows than the normal (ball-milled) cement. This indicates that reduction of the maximum particle size overcomes interparticle interference

effects and improves the mortar flow despite the fact that the pastes are stiffer, as discussed in Section 6.1. The mortar strength tests showed that their strength development is also substantially better than for the ball-milled cement:

	Clinker B.S.S. <u>cm²/g</u>	Cement B.S.S. <u>cm²/g</u>	<u>Compressive Strengths*, psi</u>		
			<u>1 Day</u>	<u>7 Days</u>	<u>28 Days</u>
PM 43	3370	3661	1875	4425	5775
PM 64	2626	3160	2000	4800	6325
PM 65	3096	3600	2700	5975	7450

*These mortars are mixed at a water-cement ratio of 0.485.

Hence, we concluded that these cements should yield good strengths as well as workable concrete mixes and we proceeded with the Series IIIa concrete tests.

The concrete mixes were designed for 2 to 4 inch slumps at water-cement ratios of 0.45 and 0.55. The measured slumps averaged about 2.2 inches. No difficulties were experienced with mixing the concretes with the particle size controlled cements, although the consistencies and appearances were somewhat different (see below); they appeared to be wetter than the concretes made with the normally ground cement. All of these low-slump concretes required vibration during casting. All the mixes flowed well with vibration.

The mix proportions, slumps, and strength data for these concretes are given in Table 20. Each concrete was mixed with a normal mixing time, after which slumps were measured and proportions adjusted (at constant w/c) to achieve the desired slump. Then a set of 3x6 inch cylinders were cast for strength

tests. The remainder of the batch was then mixed for an additional 25 minutes and a second set of specimens cast. This procedure was used to simulate extended mixing in a transit mixer to see if any grinding of the cements during extended mixing would alter the performance of the cements. In almost every case, the extended mixing resulted in higher strengths with all three cements. The only exception was with PM 65, the 20 micron maximum size, with the Elgin gravel at the higher water cement ratio.

For comparison with the ASTM C109 mortar strengths given above, the strength data for one set of concretes made with the Thornton limestone aggregate at water-cement ratios of 0.45 and 0.55 were interpolated to get the values at 0.484 water-cement ratio:

	<u>Cement Content (bags/cu yd)</u>		<u>Compressive Strength* (psi)</u>		
	<u>0.45 w/c</u>	<u>0.55 w/c</u>	<u>1 Day</u>	<u>7 Days</u>	<u>28 Days</u>
PM 43	6.84	5.60	1600	4750	6600
PM 64	8.55	6.09	1900	4700	6850
PM 65	7.66	6.25	2700	6280	7520

*Values for $w/c = 0.484$, interpolated from the two water ratios.

Most of these values may be seen to be in good agreement with the mortar tests.

In the concrete tests, cements PM 64 and 65 often yielded better strengths than PM 43, but the results were nevertheless somewhat disappointing because the cement contents were usually higher with the particle size controlled cements. Although experienced personnel made the adjustments of the proportions,

the particle size controlled cements have flow properties somewhat different from those of normal cements. Since the adjustments are based on visual observation and judgment of the operator based on experience with normal cements, the resulting mixes varied considerably in fine aggregate and cement contents, as shown in Table 20. The concretes made with the particle size controlled cements usually contained smaller percentages of fine aggregates, as well as higher cement contents. Hence, the mortar fractions were richer in cement, which was not the objective; we hoped to have cement factors no higher than with the normal cement.

More experience with the particle size controlled cements is necessary to optimize properly the mixes for economical use of such cements. The main objective of these tests was to see if there were any unanticipated problems in the use of these cements in concretes. The results show that further work on optimization of the mix designs is required. Nevertheless, workable mixes and better strengths were obtained with cements of much lower cement clinker finenesses than that of the normal particle size distribution cement.

6.3 Series IIb - Cement Paste Tests

The Series IIb tests were designed to determine the properties of cements of controlled particle size distributions with relatively low Blaine finenesses that would yield reasonable fresh paste flow properties and good strength development.

The results of the Series IIb tests are given in Tables 21 and 22. Table 21 contains the results for the high C_3A con-

tent cements made with clinker 275; Table 22 contains the data for the low C_3A content cements using clinker 274. Maximum particle size, percentage of added clinker fines, percentage gypsum, and B.S.S. values are given in the tables for comparison with the properties of the pastes made with each cement. Particle size distribution curves for three of the cements PM 38, 52, and 66 are shown in Fig. 15.

The B.S.S. areas of these particle size controlled cements were substantially less than that of the ball-milled cements used as controls. Since the gypsum makes a substantial contribution to the fineness, B.S.S. values for both the finished cements and the ground clinker without gypsum are given for each cement in the tables and in Fig. 15. Gypsum contents corresponding to sulfate to aluminate mole ratios, $\bar{S}/A$, of 0.6 and 0.8 were used with each clinker.

Bleeding. Pastes were mixed at 0.4, 0.5, and 0.6 water-cement ratios. Values of the water-cement ratios corrected for bleeding are also given for each paste. The values were calculated from the density at 1 day, d_1 , and the specific volume of the cement (0.317) from:

$$w_o/c = \frac{1 - 0.317 d_1}{d_1 - 1}$$

This assumes that the water uptake and dimensional changes after setting during the first day of moist curing are negligible. Making these assumptions yielded reasonable results. The standard deviation of the densities calculated from the mass and dimensions of the paste cubes was about 0.008 g/cm^3 which

leads to an uncertainty of the corrected water-cement ratios of about the same magnitude.

The water-cement ratios corrected for bleeding show that none of these cements differed appreciably in bleeding characteristics. The low C_3A cements bled slightly more than the high C_3A cements.

Workability. In this test series, paste workabilities were not measured by the mini-slump cone method but a visual estimate was made during mixing of each paste. These correspond to approximate mini-slump pat areas (as were given for the Series II tests) as given below:

<u>Visual Estimate</u>	<u>Pat Area (in.²)</u>
VF - very fluid	more than 17.0
F - fluid	10.0 - 17.0
VW - very workable	8.0 - 10.0
W - workable	2.5 - 8.0
S - stiff	less than 2.5

The results shown in Tables 21 and 22 show that almost all of the cements had the same workabilities: fluid, very workable, and workable, at 0.6, 0.5, and 0.4 water-cement ratios, respectively. The few exceptions for 275 were PM 66, 67, 52, and 53 (the 20 micron maximum particle size cements), which were somewhat stiffer at all water-cement ratios, and PM 44 (the low-sulfate 30 micron cement with the least amount of added fines), which was stiffer only at the lowest water-cement ratio. The low C_3A content 274 ball-milled grinds yielded even more workable pastes, being very fluid at 0.6 water-cement ratio. For

this clinker, PM 62 (the low sulfate 20 micron maximum particle size cement) yielded higher workabilities, the same as the ball-milled controls, contrary to the results for 275. Hence, the stiffness of the 275 pastes seems to be attributable more to the early aluminate hydration reactions than the direct physical effects of this particle size distribution.

Degree of Hydration. The degree of hydration, or the percentage of the cement hydrated at each testing age, was determined for each cement at two water-cement ratios, 0.6 and 0.4. The degree of hydration (and strength) at 28 days was determined for two curing conditions, moist cured and sealed cured (which permits some self-desiccation). These values were calculated from the non-evaporable water contents determined by loss on ignition after the hydrated samples were dried to constant weight in vacuum at a water vapor pressure controlled by an ice trap at -79°C (dry-ice temperature). This drying procedure is called D-drying and such samples are referred to as D-dried. To calculate the degree of hydration, one must know the non-evaporable water content per gram of ignited cement (w_n/c_i) for completely hydrated cement pastes. This value for each cement (w_n/c_i)_u is determined by examination of the plots of w_n/c_i vs. log (curing time) to estimate the ultimate value. The best estimates are obtained with the most finely ground cements at high water-cement ratios cured for the longest times. The plots for the high C_3A clinker 275 showed that hydration of the finest cements (PM 48, 52 and 66) proceeds much more rapidly at early ages than the ball-milled cements, after which the rate

of increase decreases, and perhaps ceases entirely because the cement is completely hydrated. The plots indicated a value of 0.240 for w_n/c_i for the completely hydrated 275 cements which was used to calculate the percentage hydrated in the partially hydrated specimens. The degrees of hydration data show the retarding effect of the dense hydrates formed in low water-cement ratio pastes on the hydration of the remaining cement.

Similar results were obtained for the 274 (low C_3A) cements. These cements hydrated more slowly and at 28 days even the finest cements had not yet completely hydrated. However, at 60 days it appears that these finest grinds may be nearly completely hydrated and the value of 0.208 was used to calculate the degree of hydration values given in Table 22.

Strengths. The strength development at various ages and water-cement ratios clearly show the effects of variations in the water-cement ratios and the degree of hydration of the hardened pastes. For easier comparisons, representative strength data are plotted in Figs. 16 and 17. These plots show that in almost every case the strengths of the particle size controlled cements equal or exceed the strengths of the ball-milled cements even at early ages although the B.S.S. values are substantially lower than those for the ball-milled cements. One interesting result is that whereas the ball-milled cements have optimum strength development at gypsum contents corresponding to a sulfate-to-aluminate ratio ($\bar{S}/A$) of about 0.6, and usually have lower strengths at $\bar{S}/A$ of 0.8, the particle size controlled cements often have better strengths at $\bar{S}/A$ of 0.8. In a few cases, the less than 20 micron 275 cements with

5.7% gypsum at low water-cement ratios at 7 and 28 days, the particle size controlled cements failed to exceed the strength of the controls. Since this reduction was not as great at 7.6% gypsum, it appears these cements were undersulfated; even at 7.6% gypsum (sulfate to aluminate ratio of 0.8), they may have been undersulfated.

Examination of the data also shows that for the 30 micron maximum size particle cements, the Blaine finenesses must be somewhat higher than in the 20 micron maximum particle size cements in order to equal the 1-day strengths of the ball-milled cements. The results may be summarized as follows:

B.S.S. Values (cm^2/g) at Which the Particle Size
Controlled Cements Equal the 1-Day Strengths
of the Ball-Milled Cements

$\bar{S}/A$	275 (12% C_3A)		274 (7% C_3A)	
	0.6	0.8	0.6	0.8
30 microns	3329	3460	<3301 >3061	3241
20 microns	3229*	<3250 (3100?)	2856	2928
B.S.S. of ball-milled cements	3802	3938	3566	3708

*undersulfated

Hence, it appears that the B.S.S. values of the less than 30 micron cements are about $450 \text{ cm}^2/\text{g}$ lower than the controls for equal 1 day strengths. The Blaine finenesses of the less than 20 micron 275 cements at $\bar{S}/A = 0.8$ is higher than required;

the strengths were greater than the controls. A value of perhaps $3100 \text{ cm}^2/\text{g}$ would probably have sufficed. For the 20 micron maximum size, the required Blaine finenesses are 700-800 cm^2/g lower than the controls.

The particle size distribution data given in Table 6 shows that in addition to the differences in maximum particle sizes and Blaine finenesses there is another principal difference between these cements and the normally ground cements. The normal grinds have 20-25% finer than 5 microns and 8-11% finer than 2 microns. The particle size controlled cements have about 16-25% finer than 5 microns, but only 3-5% finer than 2 microns.

It is also apparent that much of the improved strength of the particle size controlled cements is a result of their higher degree of hydration at ages equal to those of the ball-milled cement controls. There are also some variations in the corrected water-cement ratios that lead to uncertainties in such comparisons. In order to compare these cements on a basis which accounts for both of these variations, so that we can more clearly see the effects of the particle size distribution control, we have calculated the gel-space ratio, G/S, for each hardened paste for which the degree of hydration was determined.

Gel-Space Ratio and Strength. The G/S ratio is the fraction of the available space (outside the unhydrated cores of the cement particles) which is filled with hydration products. To calculate this, we assumed that at a water-cement ratio of 0.38, a completely hydrated paste would have zero capillary porosity

and a G/S ratio of 1.0. The equation based on this assumption (for clinker 275) is:

$$G/S = \frac{2.99}{w_o/w_n + 1.34}$$

These calculated values are given in Table 23. Prior work has shown that the compressive strength, f_c , is related to the G/S ratio by:

$$f_c = f_{co} (G/S)^n$$

where f_{co} is the intrinsic strength of the cement gel and n is a constant with a value of about 3.0. This equation was tested with the ball-milled 275 cements by plotting $\log f_c$ vs. $\log G/S$; linear plots were obtained with slopes that yielded values of n ranging from 2.73 to 3.23, the low water-cement ratios yielding slightly lower values than the high water-cement ratios. Using a value of $n = 3.0$, these strength data are plotted against $(G/S)^3$ in Fig. 18. The values for f_{co} indicated by the intercepts at $G/S = 1.0$ for the two corrected water-cement ratios (0.545 and 0.387) do not agree and are:

$$f_{co} = 19,400 \text{ psi at } w_o/c = 0.357$$

$$f_{co} = 14,000 \text{ psi at } w_o/c = 0.545$$

Gypsum content variation showed no measurable effect on f_{co} , but did affect w_n at equal ages. In the published work of T. C. Powers, who originated the gel-space ratio concept, it was assumed that there was a single value of f_c for each

cement, and this was verified by experimental work. However, the scatter of that data was considerable and the data was somewhat limited. These data show little scatter and cover a wide range of both w_o and w_n values. The plots clearly reveal that higher strengths are obtained at a water-cement ratio of 0.387 than at 0.545 at equal gel-space ratios.

Utilization of the Cement for Strength. The implication is that the cement is being more efficiently utilized for strength development at low water-cement ratios than at higher water-cement ratios, as was suggested from theoretical considerations in the proposal for this work (see Fig. 4 in the proposal). There it was calculated that at water-cement ratios of 0.38 and 0.55, only 76% and 66%, respectively, of the cement was fully utilized for strength because the finest particles were too small to fill their water-films with dense cement gel. This concept appears to be consistent with the results in Fig. 18.

We can make a quantitative estimate of the difference in the percentages of the cement utilized from the positions of the two straight lines in Fig. 18. First the value of $(G/S)^3$ for the fully hydrated pastes were calculated to be 0.994 and 0.540 for the upper and lower lines, respectively. These are indicated by points A and C. Point C has a much lower strength than indicated by Point B at the same gel-space ratio on the upper line, indicating more of the cement, although hydrated, did not contribute to strength. To estimate how much more, we use the lower w/c line to determine the $(G/S)^3$ value required to obtain the same strength as at Point B (10,500 psi). This

value is 0.746, which corresponds to a G/S ratio of 0.907 to obtain this strength when the cement is less efficiently utilized. At this water-cement ratio (0.545), this corresponds to a fictitious cement content c' , greater than at c . This fictitious cement content is calculated from $G/S = 0.907$, which yields a w/c of 0.458. Then the amount of cement not utilized is:

$$\begin{aligned}\frac{\Delta c}{w} &= \frac{c'}{w} - \frac{c}{w} \\ &= \frac{1}{0.458} - \frac{1}{0.545} \\ &= 2.18 - 1.83 = 0.35\end{aligned}$$

Then

$$\frac{\Delta c}{c'} = \frac{0.35}{2.18} = 0.16 = 16\%$$

That is, only 84% of the cement utilized at $w/c = 0.387$ is utilized at $w/c = 0.545$. Then if, as calculated from the theoretical considerations in the proposal, only 76% of the cement is utilized at $w/c = 0.387$, only

$$0.76 \times 0.84 = 0.64 = 64\%$$

is utilized at $w/c = 0.545$. Hence, these values are in very good agreement with our earlier theoretical predictions.

We are now in a position to examine the particle size distribution effects at equal G/S ratios, which eliminates the complicating effects of variations in w/c and w_n/c or degree of hydration. These results for some of the 275 cements are plotted in Figs. 19 and 20. In these cases the data points for the particle size controlled cements are slightly below the

straight lines for the ball-milled controls which are shown for comparison. For some of these high C_3A cements, the <30 micron cements at $\bar{S}/A = 0.6$ at $w/c = 0.4$, and the <20 micron cements at $\bar{S}/A = 0.6$ and 0.8 at $w/c = 0.4$, similar plots show that the strengths are significantly less than that of the ball-milled controls. This implies that in such cases the cements are being utilized for strengths less efficiently than in the pastes made with the ball-milled cements with broad particle size distributions. This is somewhat surprising and indicates that the superior strengths at equal ages is entirely a result of the more rapid and more complete hydration of these cements. In the other cases, the particle size controlled cements yielded strengths equal to or only very slightly below those of the controls at equal G/S ratios. In a very few cases, they are slightly higher.

Hence, we have not yet succeeded in producing significantly better distribution of the hydration products to produce cement gels of intrinsically higher strength, one of the objectives of the study. This may be a result of the restrictions imposed on the particle size distributions to lower the water requirement for flow of the fresh pastes. Nevertheless, we have achieved much more efficient utilization of the cement for strength by the more rapid and more complete hydration of these cements at all ages.

Drying Shrinkage. Drying shrinkage of thin 3 mm slabs of each cement paste was measured at 52% relative humidity after 7 and 28 days of moist curing. Such thin slabs reach approximately constant length during this drying in about 4 weeks.

The results in Tables 21 and 22 show that for all of the cements, the shrinkage increased with water-cement ratio and curing time, or degree of hydration. Since the particle size controlled cements are more completely hydrated at each curing time, their shrinkages are often greater than that of the controls. Nevertheless, there are some exceptions to this rule. In 8 out of 60 cases, the shrinkages were less than the controls with the high C_3A cements. In 13 out of 60 cases, the shrinkages were less than the controls with the low C_3A cements.

Most of these cements had higher fines contents than required to exceed the early strengths of the controls. There are some indications that the shrinkage increases with the amounts of fines in the particle size controlled cements, but there are also exceptions to this. These exceptions indicate that in these cases we have improved the distribution of hydration products to reduce the drying shrinkage even at higher degrees of hydration. Since these pastes were also stronger their shrinkage cracking tendencies should be less.

It was also found that the shrinkage increased less with water-cement ratio and was much less at high water-cement ratios at the 0.8 sulfate-to-aluminate ratio than at 0.6. For the ball-milled cements, strengths were less at 0.8 than at 0.6, but for the particle size controlled cements, the reverse was often true. There seems to be better agreement between the optimum gypsum for strength and that for shrinkage for the particle size controlled cements than for the ball-milled cements.

7. Effects of Mixing and Curing Temperature

The Series IV tests were designed to compare the properties of several good particle size controlled cements with normally ground cements at low and high temperatures. Temperatures of 42°F and 100°F were used to simulate winter and summer outdoor temperatures. The same two, low and high C₃A content, cement clinkers (274 and 275) used in Series II and III were used. Three gypsum contents corresponding to sulfate to aluminate mole ratios of 0.4, 0.6, and 0.8 were used for each clinker. Pastes were made at only one water-cement ratio of 0.5. The cements were similar to those used in Series III. PM 50, 51, 60, and 61 contained 10% added fines, a little less than the 15% used for the comparable blends in Series III. The blend proportions, Blaine finenesses, fresh paste workabilities, and the compressive strength data, are shown in Table 24. The Blaine finenesses of the particle size controlled cements were 200-500 cm²/g less than the ball-milled cements.

We also included in this series two blends with 10% ground Iowa limestone (designated A-140) replacing the cement fines. This material was Vortec classified to yield a fine fraction of 6 microns maximum particle size and 12992 cm²/g Blaine. The Blaine values given are for the pebble mill blends PM 70 and 71 before the addition of the A-140 limestone fines. The limestone was added to these cements at the time of mixing. The B.S.S. values of these blended cements would therefore be about 1000 cm²/g higher than the values given for the PM blends if we consider the contribution of the A-140 fines, and would have

to be included in the calculation of the average water-film thicknesses for these pastes.

The particle size controlled cement pastes were all a little less workable, or had a slightly higher water requirement, than the pastes made from the normally ground cements PM 42 and 43.

No tests could be made at 1 day at 42°F because none of the pastes had set. Instead, we tested these cubes after four days of curing, at which time the degree of hydration was estimated to be about the same as at 1 day at 73°F.

In Table 24, we have also included for comparison compressive strength data from other test series at 73°F. Also, we did not test the high sulfate content pastes at 42°F or the low sulfate pastes at high temperatures because it is known that at low temperatures less sulfate can be tolerated (expansion may result) and that more sulfate is required at high temperatures. See, for example, PM 42 cured at 100°F for 28 days; also compare PM 50 and 51, which shows much higher strengths at the higher sulfate content when cured at 100°F for 28 days.

The particle size controlled cements usually yielded considerably higher strengths than the normally ground cements. In some cases, the strengths were about the same; in only four cases were they somewhat lower: the low sulfate-high C_3A PM 73 (which contained no added clinker fines) at 4 days at 42°F, and the 7 day strengths of PM 51, PM 70, and PM 71 at 100°F. These three had high sulfate or carbonate additions. However, at 28 days, two of these cements yielded outstandingly

high strengths; they were PM 51 and PM 70, the high C_3A cement at high sulfate content, and with the carbonate addition. Perhaps these cements were also slightly expansive, which might account for the lower strengths at 7 days.

At low temperatures the cements with limestone replacements were even better than the particle size controlled cement without limestone, as well as the ball-milled cement, for each of the two cement clinkers (high and low C_3A) studied at all ages. These results are most interesting and should provide opportunities for further improvements in the performance of such blended cements and a potential for even more energy savings.

It should be noted that not only was 10% of the cement replaced with limestone in these mixes, but that the water-solids ratio was kept constant at 0.5. Hence, the actual water-cement ratios were higher, 0.55. Despite the higher water-cement ratios, the hardened pastes with carbonate were usually stronger than the controls at both high and low temperature.

8. Effects of High-Alkali and High-Sulfate

Contents in Cement Clinker

Chemical analyses of the two cement clinkers selected for the Series V tests were given in Table 1. Clinker 14K2 is a high alkali clinker with 1.37% K_2O and 0.04% Na_2O . Clinker 280 has both a high-alkali content and a high-sulfate content characteristic of clinkers made by burning high-sulfate fuels. It contained 1.10% K_2O , 0.10% Na_2O , and 1.33% SO_3 .

The cements were made using the same procedures used for preparation of the cements for Series II, III and IV. They were prepared with gypsum contents corresponding to sulfate to aluminate mole ratios of 0.4, 0.6 and 0.8. T.A.5 gypsum was again used in these cements. The total SO_3 including that of the cement clinker was used for the sulfate to aluminate ratios in the cements. The percentage of fines added to the less than 30 micron Vortec mill product, the gypsum contents, and Blaine finenesses are given for these cements in Table 25 along with the data on the paste properties. Loss on ignition data are also given for the lowest gypsum content cements.

Workability. The cement pastes were mixed at a water-cement ratio of 0.5. Workability of the fresh pastes was estimated as in Series III and IV, and also minislump pat areas were measured. As may be seen by comparison with the table of corresponding values given in Section 6.3, these pat areas are often lower than the values corresponding to the visual estimates given in that table. Since the values used to construct the table were for the low alkali and low sulfate clinker cements (274 and 275) this suggests that the high alkali and sulfate content clinkers produced cement pastes of somewhat different rheological properties. They may have higher yield values (giving smaller pat areas) but equal plastic viscosities. The flow properties of the particle size controlled cement pastes made with clinker 14K2 were not much stiffer than those of the normally ground cement PM82. The particle size controlled cements made with the high-sulfate clinker 280 were somewhat stiffer than the normally ground controls.

Bleeding. Differences in bleeding of the particle size controlled cements and the normally ground cements were insignificant, as indicated by the values of the water-cement ratios corrected for bleeding.

Time of Set. The particle size controlled cements set somewhat faster, about 1 hour sooner, than the normally ground cements, despite their lower Blaine finenesses.

Strengths. The particle size controlled cements usually produced strengths higher than the normally ground cements. The data show the complicating effects of the high alkali contents on the gypsum requirements. Neither normally ground cement showed an optimum gypsum content for maximum strength at 1 day, but the 14K2 cements did at 28 days at $\bar{S}/A$ of about 0.6. The 14K2 cements with only 5% added fines (PM86, 86-87, and 87) did not perform very well at any gypsum content, having low strengths at some age for all three gypsum contents. However, with 15% added fines the cements substantially exceeded the strengths of the controls at the highest gypsum content. The high-sulfate cements 280 also performed better with 15% added fines, yielding higher strengths than the controls at the highest gypsum content.

As with the low alkali and sulfate content clinkers 274 and 275 these particle size controlled cements also exceeded the 1 day strengths of the normally ground cements at considerably lower Blaine finenesses. For 280 the B.S.S. values were about $700 \text{ cm}^2/\text{g}$ lower for greater 1 day (and later) strengths. For 14K2 the B.S.S. values were at least $275 \text{ cm}^2/\text{g}$ lower for greater strengths. It appears from the data that the fines

contents and the Blaine fineness could have been further reduced and still have exceeded the strength of the controls.

Although these high alkali and sulfate content clinkers show somewhat more complicated behavior than the 274 and 275 cements similar improved proved performances were achieved with particle size control. In fact, since we used 30 micron maximum size particle cements in these tests we did not fully exploit this potential. If we had used a maximum particle size of 20 microns it is almost certain that even better performance would have been obtained, as was the case with the other two clinkers. Additional work should be done to verify this. At present there is no indication that these clinkers behave very differently in this respect.

9. Estimates of Energy Conservation Potential of Cement Particle Size Control

9.1 Grinding Energy

The most immediate energy conservation potential of cement particle size control as developed in this research program, is that of grinding energy savings. Such estimates must be based on information derived from use of conventional equipment, or based on more limited information for newer types of equipment not yet in common use.

In the proposal for this work (p.4) an estimate was made, based on the use of conventional closed circuit milling systems. This estimate was based on the assumptions 1) that such equipment could (with modification) produce the desired particle size distributions and 2) the desired product would have a

Blaine fineness of only $2600 \text{ cm}^2/\text{g}$ and still equal the performance of normally ground cements of about $3600 \text{ cm}^2/\text{g}$. The results obtained in this study have shown that the best cements we have made have maximum particle sizes of about 20 microns, and that these exceed the strengths of normally ground cements with $700 - 800 \text{ cm}^2/\text{g}$ lower Blaine finenesses.

Type I cements now usually produced in the United States require about 45 kwh/ton for finish grinding. About 1 kwh/ton is required to produce $65 \text{ cm}^2/\text{g}$ of additional surface at $2800 \text{ cm}^2/\text{g}$. Hence at $2800 \text{ cm}^2/\text{g}$ about 12 kwh/ton or 27% of the grinding energy would be saved. Considering the conversion of thermal to the electrical energy required this is the equivalent of $12 \text{ kwh/ton} \times 10,600 \text{ Btu/kwh} = 127,000 \text{ Btu/ton}$. For an annual production of 75 million tons in the U.S. this should save $9.5 \times 10^{12} \text{ Btu/year}$, or $9.5 \times 10^9 \text{ MJ/year}$.

It must be recognized that existing installations would require considerable improvement in the classification efficiency of the air separators used to separate out the coarse fraction for return to the mill. Much sharper particle size classification is required than normally achieved by existing equipment. However, if such improved (and presumably more expensive) classifiers were used the mill efficiencies would be improved because the circulating load of fines in the mills would be reduced. This should result in further energy savings.

Another alternative is the use of new types of grinding mills such as the Loesche Roller Mill. Such air-swept mills are intrinsically more efficient than conventional ball mills.

Grinding tests have shown that the power requirements for grinding cement in a roller mill are about 10% less than in other grinding systems (Rock Products, Aug. 1978, pp. 60-62).

9.2 More Efficient Utilization of the Cement

An even greater potential for energy conservation should result from the fact that the cement clinker is more efficiently utilized for strength development in particle size controlled cements. The concrete data in this study did not provide an adequate basis for making such an estimate because all of the mixes were not properly proportioned for economical use of the cements. However, the mortar and cement paste data both indicated more efficient utilization of the particle size controlled cements. The energy savings may be conservatively estimated as follows. Taking, for example, the data of Figure 17 for the PM 69 (less than 20 microns) and PM41 (normally ground) cements we see that for equal 28 day strengths of 7000 psi the normally ground cement would have a water-cement ratio of 0.45 while the less than 20 micron cement would have a water-cement ratio of 0.52. The mass of cement, c , is related to the paste volume V by:

$$\frac{c}{V} = \frac{1}{v_c + w_o/c}$$

For the above water-cement ratios this yields cement contents per unit of paste volume of 1.30 g/cc at 0.45, and 1.19 g/cc at 0.52 water-cement ratio. Then for equal volumes of equally strong hardened cement 0.11 g/cc or 8.5% less cement would be used. Since about 6 million Btu/ton is required to produce the cement clinker in conventional kiln systems this

would result in additional savings of 0.5 million Btu/ton, nearly four times the grinding energy savings. This would result in an annual energy consumption reduction of 37×10^{12} Btu/year or 37×10^9 MJ/year.

This estimate is actually rather conservative because the higher water cement ratio would result in a more workable concrete. Since concrete mixtures are designed for slumps required for placement the amount of cement paste and cement could be further reduced, its volume being replaced by sand and coarse aggregate. Alternatively, less water could be used to obtain higher strengths.

9.3 Blended Cements

Perhaps the greatest potential for energy conservation lies in the use of blended cements in which some of the cement clinker is replaced by readily available ground materials such as limestone, slags, sands, etc. Cement plants usually have limestone deposits (sometimes oyster shells are used as the calcareous raw material). Sometimes these deposits contain seams of dolomitic rock which is undesirable for cement manufacture because of the risk of deleterious expansive reactions of the MgO in the resulting clinker. Such rock must sometimes be discarded, but could just as well be used as an inert addition. The data in Table 24 show that blends containing at least 10% ground limestone in carefully prepared blends produced better strengths than normally ground cements, even when the actual water-cement ratios were higher. This would lead to even greater energy savings than estimated in the above for particle size controlled cements alone.

9.4 Other Considerations

In addition to the above direct energy conservation potentials there are some indirect benefits that should accrue from the widespread use of particle size controlled cements instead of normally ground cements. Many benefits should result from the use of a more predictable product. Much higher early strengths have been shown to be possible with such cements. This would have ramifications with respect to both the design of concrete structures (permitting thinner and lighter structural members) and reduced construction time, energy, labor, and costs. The impact on these practices is difficult to estimate quantitatively, but since portland cement is used so widely in construction it would be unlikely that we could overestimate the potential benefits to the nation that could accrue from the replacement of normally ground cements with particle size controlled cements of the kind developed in this work.

10. Summary of Conclusions

In the above discussions many conclusions have been drawn from the results obtained in the experimental work. The most important of these are:

1. The fineness of the gypsum in cements, in which the gypsum is normally interground with the clinker, is very high (at least $12000 \text{ cm}^2/\text{g}$) and makes a substantial contribution to the measured Blaine fineness of the cements.
2. The behavior of interground cements can be approximately duplicated by cements in which the clinker and

gypsum are separately ground and then adequately blended if the fineness of the gypsum is sufficiently high (about 12000 cm^2/g).

3. The amount of ground clinker in the 2-5 micron particle size range has large effects on the bleeding, water requirement for flow, and strength development.
4. Progressive reduction of the maximum particle size to 20 microns improved strength development. Reduction to about 14 microns decreased rather than increased strength development.
5. Particle size controlled cements of 20 and 30 micron maximum particle size and Blaine finenesses ranging from 2850 to 3900 cm^2/g had about the same or only slightly higher water requirements for flow of the fresh pastes than the normally ground cements.
6. Some of these particle size controlled cements produce as high (and often much higher) strengths at ages from 1 to 60 days at Blaine finenesses substantially lower (450 to 800 cm^2/g) than the normal grinds of the same composition.
7. The less than 30 micron cements have Blaine finenesses about 450 cm^2/g less than the normally ground cements for equal 1 day strengths. The less than 20 micron cements have Blaine finenesses 700 to 800 cm^2/g less than the controls for equal 1 day strengths. These cements have only 3-5% finer than 2 microns.

8. The superior strength development of these particle size controlled cements is due to the more rapid and more complete hydration of the cement.
9. For all of the hardened cements, the drying shrinkage increased with the water-cement ratio and curing time, or degree of hydration.
10. Because of their higher degrees of hydration, most of the particle size controlled cements had shrinkages greater than the controls. However, some shrank less, despite the higher degree of hydration, indicating that in these cases we have improved the hardened paste structure by particle size control so as to reduce the shrinkage. Since they were also stronger their shrinkage cracking tendencies should be less.
11. Drying shrinkage varied much less with water-cement ratio and was much smaller at higher water-cement ratios at a sulfate to aluminate mole ratio of 0.8 than at 0.6 for all of the cements.
12. For the ball-milled cements, strengths were less at a sulfate to aluminate mole ratio of 0.8 than at 0.6, but for the particle size controlled cements the reverse was often the case; particle size controlled cements seem to be able to tolerate higher sulfate contents without loss of strength.
13. The optimum gypsum content for strength agrees better with that for drying shrinkage for the particle size controlled cements than for normally ground cements.

14. The above conclusions apply equally well to high and low C_3A content clinkers. The conclusions with respect to strength development also apply to clinkers with high alkali and sulfate contents. The behavior of the high alkali cements was somewhat irregular, but there is no indication from this work that the particle size distributions required for best performance depended significantly on the clinker composition.
15. Tests at $42^{\circ}F$ and $100^{\circ}F$ (as well as at $73^{\circ}F$) with high and low C_3A content cements showed that the particle size controlled cements usually performed better over this temperature range. The cements that did not contained deliberately high and low sulfate or carbonate additions.
16. At low temperatures the particle size controlled cements with limestone replacements for cement clinker were even stronger than the same cements without limestone, despite the fact that their actual water-cement ratios were higher (0.55 vs 0.50).
17. Limited tests of mortars and concretes confirmed that superior performance of the particle size controlled cements.
18. It is estimated that if universally adopted by the U.S. cement industry cement particle size distribution control could result in energy usage savings of:
 - a. 27%, or 9.5×10^{12} Btu/yr. in grinding energy,

- b. 8.5%, or 37×10^{12} Btu/yr. in kiln fuel energy by more efficient utilization of the cement,
- c. at least 10% in kiln fuel energy if particle size controlled cements are used in blended cement, and
- d. other indirect savings.

Fig. 1 Simple model of the structure of fresh cement paste for a normally ground cement. Each particle is assumed to be covered by a water film of approximately equal thickness. The largest particle shown has a diameter of 30 microns; the smallest, a fraction of a micron.

Fig. 2 Particle size distribution in curves for two normally ground cements of two different Blaine finenesses, and three idealized distribution curves with maximum particle sizes of 45 and 20 microns.

Fig. 3 Particle size distribution curves of cement clinker ground separately in the Vortec Impact Mill.

Fig. 4 Particle size distribution curves of cement clinker ground with the M-1 Vortec Impact Mill and C-13 Classifier system operating in closed circuit at different throttle settings.

Fig. 5 Particle size distribution curves of blends of different size fractions proportioned to approximate two idealized size distributions.

Fig. 6 Compressive strengths of hardened cement pastes blended with Terra Alba gypsum at three different finenesses. Also shown are data for cements in which the gypsum was interground with the clinker in a ball mill. Clinker 275 (high C_3A).

Fig. 7 Dependence of the mini-slump pat areas on the average water-film thickness for four idealized particle size distributions (20-2, 45-2, 14-5 and 45-5 micron size ranges) and one normally ground cement with interground gypsum. Water-film thickness is calculated by dividing the water-cement ratio by the Blaine fineness. Clinker 275 (high C_3A).

Fig. 8 Dependence of the mini-slump pat areas on the mass percentage of particles finer than 5 microns for the four idealized particle size distributions in Fig. 7. Clinker 275 (high C_3A).

Fig. 9 Dependence of the mini-slump pat areas on the water-cement ratio for four idealized particle size distributions and one normally ground (100-0 microns) cement clinker. All cements were made by blending ground clinker with gypsum. Clinker 275 (high C_3A).

Fig. 10 Dependence of mini-slump pat areas on the average water-film thickness for cement pastes made with idealized particle size distributions and one normally ground cement clinker, at three different gypsum contents. Blaine finenesses are given in parentheses. Clinker 275 (high C_3A)

Fig. 11 Compressive strengths of hardened cement pastes at 1 day and 28 days for two idealized particle size distributions and the ball-milled controls, all blended with 7.6% gypsum. Clinker 275 (high C_3A).

Fig. 12 Compressive strengths of hardened cement pastes at 1, 7 and 28 days for two other idealized particle size distributions and the ball-milled controls, all blended with 7.6% gypsum. Clinker 275 (high C_3A).

Fig. 13 Dependence of the mini-slump pat areas on the water-cement ratio for cements with 45 and 20 micron maximum size particles with intermediate amounts of added clinker fines. Also shown are data for the ball-milled controls (100-0 microns) and Blaine finenesses for each cement. Clinker 274 (low C_3A).

Fig. 14 Compressive strengths at 1 day and 28 days of hardened cement pastes made with cements with 20 micron maximum size particles with intermediate amounts of clinker fines. Also shown are data for the ball-milled controls (100-0 microns). Clinker 274 (low C_3A).

Fig. 15 Particle size distribution curves for two particle size controlled cements (PM 52 and PM 66) and the ball-milled control (PM 38). Blaine finenesses are shown for the ground clinker without gypsum and for the finished cements. Clinker 275 (high C_3A).

Fig. 16 Compressive strengths at 1, 7 and 28 days for hardened cement pastes made with three cements of 30 micron maximum size particles (PM 45, 47 and 49) and the ball-milled controls (PM 39). Clinker 275 (high C_3A).

Fig. 17 Compressive strengths at 1, 7 and 28 days for hardened cement pastes made with two cements with 20 micron maximum size particles (PM 69 and PM 63) and the ball-milled controls (PM 41). Clinker 274 (low C_3A) with 5.2% gypsum.

Fig. 18 Compressive strengths, f_c , of hardened cement pastes made with normally ground^c clinker with two gypsum contents (PM 38 and 39) at two water-cement ratios and cured for 1, 7, 28 and 60 days. Strengths are cubic functions of the calculated gel space, G/S . Points B and C give the strengths at the gel-space ratio of the completely hydrated higher w/c pastes. Point C' gives the (fictitious) gel space ratio required at the higher w/c to yield the same strength of the lower w/c. Clinker 275 (high C_3A).

Fig. 19 Compressive strengths, f_c , of hardened cement pastes made with less than 30 micron cements with an original water-cement ratio of 0.4 and cured for 1, 7, 28 and 60 days, plotted as a function of the calculated gel-space ratios, G/S . The straight line is that for the ball-milled controls. Clinker 275 (high C_3A) with 7.6% gypsum.

Fig. 20 Compressive strengths, f_c , of hardened cement pastes made with less than 30 micron cements with an original water-cement ratio of 0.6 and cured for 1, 7, 28 and 60 days, plotted as a function of the calculated gel-space ratios, G/S . The straight line is that for the ball-milled controls. Clinker 275 (high C_3A) with 7.6% gypsum.

TABLE 1

Potential Compound Compositions, Quantitative XRD
Phase Compositions, and Oxide Analyses of Portland
Cement Clinkers (Percentages)

	274		275		280		14K2	
	Potential	QXRD	Potential	QXRD	Potential	QXRD	Potential	QXRD
C ₃ S(alite)	59.79	75.36	61.22	68.44	51.30	57.02	47.1	51.28
C ₂ S(belite)	19.18	18.67	15.38	21.35	23.67	30.22	29.9	19.82
C ₃ A	6.85	1.88	12.11	7.56	11.00	5.79	8.1	2.59
C ₄ AF(F _{SS})	9.46	8.44	7.73	4.15	7.91	7.18	9.2	7.73
Na ₂ SO ₄			0.04		0.23			
K ₂ SO ₄			0.13		2.03			
CaSO ₄					0.45			
	Oxides		Oxides		Oxides		Oxides	
SiO ₂	22.42		21.47		21.75		22.8	
Al ₂ O ₃	4.57		6.19		5.81		5.0	
Fe ₂ O ₃	3.11		2.54		2.60		3.0	
CaO	65.82		67.26		64.91		63.7	
MgO	2.93		1.26		1.72		2.7	
SO ₃	0.34		0.08		1.33		0.4	
Na ₂ O	0.08		0.14		0.10		0.04	
K ₂ O	0.40		0.14		1.10		1.37	
Free CaO	0.63		1.02		-		0.3	
L.O.I.							0.6	

TABLE 2

Oxide Analyses of Several Particle Size Fractions
of Cement Clinker 274 (Percent)

Size Fraction (microns)		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	L.O.I.
<45	XRF	22.40	4.28	3.01	66.11	3.06	0.08	0.08	0.38	0.35
	AA		4.47	3.13				0.08	0.38	
	Leco						0.23			
<20	XRF	22.18	4.28	3.03	66.15	3.07	0.08	0.08	0.38	0.26
	AA		4.47	3.13				0.08	0.37	
	Leco						0.22			
14-5	XRF	22.62	4.31	3.06	65.96	3.18	0.02	0.08	0.34	0.37
	AA		4.50	3.14				0.08	0.33	
	Leco						0.14			
8-1	XRF	22.26	4.28	3.08	65.66	2.99	0.20	0.11	0.48	0.84
	AA		4.44	3.16				0.09	0.48	
	Leco						0.32			
100-0 (Ball-Milled)	XRF	22.76	4.33	3.24	65.63	3.06	0.12	0.13	0.43	0.67
	AA		4.48	3.37				0.10	0.43	
	Leco						0.23			
	AA*	22.42	4.57	3.11	65.82	2.93	0.34	0.08	0.40	

*Original analysis of whole clinker.

TABLE 3

Oxide Analyses of Several Particle Size Fractions
of Cement Clinker 275 (Percent)

Size Fraction (microns)		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	L.O.I.
<45	XRD	21.56	6.25	2.20	67.50	1.23	0.00	0.13	0.16	0.35
	AA		6.48	2.31				0.15	0.16	
	Leco						0.02			
<20	XRD	21.51	6.11	2.24	67.31	1.22	0.02	0.16	0.32	0.55
	AA		6.21	2.34				0.15	0.17	
	Leco						0.03			
14-5	XRD	21.67	6.24	2.28	66.24	1.27	0.29	0.22	0.59	0.38
	AA		6.38	2.34				0.15	0.16	
	Leco						0.01			
8-1	XRD	21.25	6.14	2.30	67.49	1.18	0.00	0.13	0.17	0.94
	AA		6.40					0.15	0.17	
	Leco						0.02			
100-0	XRD	21.46	6.12	2.30	67.58	1.19	0.00	0.13	0.16	0.44
	AA		6.27					0.15	0.16	
	Leco						0.02			
	AA*	21.47	6.19	2.54	67.26	1.26	0.08	0.14	0.14	--

*Original analysis of whole clinker.

TABLE 4

Particle Size Distributions of Terra Alba Gypsum
of different finenesses used in the cements

	90% Size Range (Microns)	Cumulative Mass Percent Finer Than Particle Sizes Indicated (microns)								B.S.S. cm ² /g
		100	50	20	10	5	2	1	0.5	
T.A. 1	50-2.2	98	95	52	27	12	4	2	0	3533
T.A. 2	47-1.0	98	96	69	47	28	13	5	1	11856
T.A. 3	44-0.8	98	96	76	55	37	18	7	1	7835 (a)
T.A. 4	16-0.9	99	99	98	73	42	19	7	1	7573
T.A. 5	40-0.7	99	99	77	58	39	22	11	2	11448 (b)

(a) The Specific Surface area calculated from the PSD curve was 7548 cm²/g. The apparent B.S.S. calculated from the PM Blend B.S.S. values averaged 8500 cm²/g.

(b) After passing 200 mesh sieve, the apparent B.S.S. values calculated from the PM Blend B.S.S. values averaged 12700 cm²/g.

TABLE 5

Particle Size Distributions of Portland Cements used in Tests
of the Effects of Gypsum Fineness and Blending Methods
Clinker 275

Cement	Test Series	Gypsum	90% Size Range (Microns)	Cumulative Mass Percent Finer Than Particle Sizes Indicated (microns)							B.S.S. cm ² /g
				100	50	20	10	5	2	1	
V1-V15	I	(a)	54-1.3	97	94	67	42	23	10	3	3472 (b)
MB1	II (Preliminary)	5.7 (c)	34-2.3	99	98	75	44	26	3	0	3534
2	"	"	35-3.7	99	98	70	35	8	1	0	2183
3	"	"	14-4.8	99	99	99	55	4	1	0	2475
4	"	"	16-2.0	99	99	99	75	35	4	0	3929
5	"	"	54-1.3	97	94	67	42	23	10	3	3600 (d)
6	"	5.7 (e)	34-2.3	99	98	75	44	26	3	0	3571
7	"	"	35-3.7	99	98	70	35	8	1	0	2321
8	"	"	14-4.8	99	99	99	55	4	1	0	2410
9	"	"	16-2.0	99	99	99	75	35	4	0	3779
V16	"	5.7 (f)	14-4.8	99	99	99	55	4	1	0	2262
PMT1	"	5.7 (g)	"	"	"	"	"	"	"	"	(h)
V17	"	5.7 (i)	"	"	"	"	"	"	"	"	2277
PMT2	"	5.7 (j)	"	"	"	"	"	"	"	"	(k)

Notes for Table 5

- (a) Primary blends with T.A.1,2, and 3 at 9.5% and 0% gypsum were V-blended 1 hour; intermediate gypsum contents were prepared by manually blending mixtures of the primary blends.
- (b) B.S.S. of ground clinker without gypsum. Values for the cements were not determined.
- (c) T.A.2, 5856 cm²/g, -200 mesh, manually blended with clinker.
- (d) Calculated from B.S.S. of clinker and gypsum.
- (e) T.A. 4, less than 15 microns, 7573 cm², manually blended and -200 mesh sieved to disperse agglomerates.
- (f) T.A. 2, 5856 cm²/g, not sieved, V-blended with clinker 15 min.
- (g) T.A. 2, 5856 cm²/g, not sieved, V-blended with clinker 15 min. then pebble milled for periods ranging from 2.5 to 60 min.
- (h) Varied with pebble milling time from 2252 to 2297 cm²/g
- (i) T.A. 3, 7835 cm²/g, not sieved, V-blended with clinker 15 min.
- (j) T.A. 3, 7835 cm²/g, not sieved, V-blended with clinker 15 min. then pebble milled for periods ranging from 5 to 60 min.
- (k) Varied with pebble milling time from 2310 to 2354 cm²/g.

TABLE 6

Particle Size Distributions of Portland Cements made
by Pebble Mill Blending Milled Clinker with Gypsum*

Cement	Clinker	Milling Method	90% Size Range (Microns)	Percent Gypsum	Cumulative Mass Percent Finer Than Particle Sizes Indicated (microns)							B.S.S. cm ² /g
					100	50	20	10	5	2	1	
PM1	275	Vortec	35-2.4	3.8	97	96	77	58	29	5	1	3582
2	275	"	35-2.4	5.7	97	96	77	58	29	5	1	3624
3	275	"	35-2.4	7.6	97	96	77	58	29	5	1	3679
4	275	"	44-3.9	3.8	96	95	67	33	9	2	0	2224
5	275	"	44-3.9	5.7	96	95	67	33	9	2	0	2517
6	275	"	44-3.9	7.6	96	95	67	33	9	2	0	2409
7	275	"	15-4.8	3.8	99	98	98	59	7	2	1	2326
8	275	"	15-4.8	5.7	99	98	98	59	7	2	1	2390
9	275	"	15-4.8	7.6	99	98	98	59	7	2	1	2480
10	275	"	18-2.0	3.8	98	98	97	69	33	6	1	3577
11	275	"	18-2.0	5.7	98	98	97	69	33	6	1	3710
12	275	"	18-2.0	7.6	98	98	97	69	33	6	1	3751
13	275	Ball Mill	50-1.1	3.8	100	95	68	44	25	11	4	3893
14	275	"	50-1.1	5.7	100	95	68	44	25	11	4	4022
15	275	"	50-1.1	7.6	100	95	68	44	25	11	4	4108
16	274	Vortec	38-2.0	2.3	97	96	73	53	25	4	1	3295
17	274	"	38-2.0	3.8	97	96	73	53	25	4	1	3316
18	274	"	38-2.0	5.2	97	96	73	53	25	4	1	3456
19	274	"	33-3.3	2.3	100	100	71	34	9	2	1	2106
20	274	"	33-3.3	3.8	100	100	71	34	9	2	1	2158
21	274	"	33-3.3	5.2	100	100	71	34	9	2	1	2239
22	274	"	16-4.0	2.3	99	98	98	53	7	2	1	2265
23	274	"	16-4.0	3.8	99	98	98	53	7	2	1	2310
24	274	"	16-4.0	5.2	99	98	98	53	7	2	1	2382
25	274	"	20-2.0	2.3	99	98	95	68	33	6	1	3601

*Terra Alba gypsum TA-3 (-200 mesh) used in PM1-P37
TA-5 used in PM38-PM87

TABLE 6 (Continued)

Cement	Clinker	Milling Method	90% Size Range (Microns)	Percent Gypsum	Cumulative Mass Percent Finer Than Particle Sizes Indicated (microns)							B.S.S. cm ² /g
					100	50	20	10	5	2	1	
26	274	Vortec	20-2.0	3.8	99	98	95	68	33	6	1	3671
27	274	"	20-2.0	5.2	100	98	95	68	33	6	1	3710
28	274	Ball Mill	60-1.2	2.3	99	93	63	39	22	9	3	3620
29	274	"	60-1.2	3.8	99	93	63	39	22	9	3	3655
30	274	"	60-1.2	5.2	99	93	63	39	22	9	3	3753
31	274	Vortec	34-2.0	3.8	100	100	70	46	25	4	1	3084
32	"	"	35-2.3	"	100	100	66	39	19	4	1	2686
33	"	"	37-2.5	"	99	99	62	34	15	3	1	2533
34	"	"	15-2.2	"	100	99	98	65	20	4	1	2930
35	"	"	16-2.7	"	99	98	98	62	15	2	0	2687
36	"	"	15-3.0	"	100	99	99	59	13	2	0	2561
37	"	"	20-2.6	"	99	99	95	53	20	3	1	2970
38	275	Ball Mill	44-1.0	5.7	100	98	65	41	24	11	5	3802
39	"	"	45-1.0	7.6	100	96	66	42	24	11	5	3938
40	274	"	50-1.1	3.8	99	95	63	40	23	10	4	3566
41	"	"	44-1.5	5.2	100	97	64	41	20	8	3	3708
42	275	"	44-1.0	5.7	100	98	65	41	24	11	5	3711
43	274	"	52-1.3	3.8	100	94	62	39	22	9	3	3661
44	275	Vortec	26-2.0	5.7	100	100	80	43	21	4	1	3329
45	"	"	26-2.0	7.6	100	100	80	43	21	4	1	3460
46	"	"	26-1.9	5.7	100	100	81	47	24	5	1	3522
47	"	"	26-1.9	7.6	100	100	81	47	24	5	1	3670
48	"	"	26-2.0	5.7	99	99	82	50	26	5	1	3791
49	"	"	26-2.0	7.6	99	99	82	50	26	5	1	3898
50	"	"	18-2.0	5.7	100	100	97	55	24	5	1	3485
51	"	"	18-2.0	7.6	100	100	97	55	24	5	1	3500
52	"	"	19-1.9	5.7	99	99	97	56	24	5	1	3516
53	"	"	19-1.9	7.6	99	99	97	56	24	5	1	3647
54	274	"	27-2.2	3.8	100	100	78	43	19	4	1	2892
55	"	"	27-2.2	5.2	100	100	78	43	19	4	1	3042
56	"	"	26-2.3	3.8	100	100	80	45	22	4	1	3061

TABLE 6 (Continued)

Cement	Clinker	Milling Method	90% Size Range (Microns)	Percent Gypsum	Cumulative Mass Percent Finer Than Particle Sizes Indicated (microns)							B.S.S. cm ² /g
					100	50	20	10	5	2	1	
57	274	Vortec	26-2.3	5.2	100	100	80	45	22	4	1	3241
58	"	"	27-2.2	3.8	99	99	78	48	23	4	1	3301
59	"	"	27-2.2	5.2	99	99	78	48	23	4	1	3348
60	"	"	19-2.0	3.8	100	100	97	55	23	5	1	3369
61	"	"	19-2.0	5.2	100	100	97	55	23	5	1	3402
62	"	"	19-2.0	3.8	100	100	97	55	24	5	1	3414
63	"	"	19-2.0	5.2	100	100	97	55	24	5	1	3460
64	"	"	26-2.3	3.8	100	100	80	45	22	4	1	3160
65	"	"	19-2.0	3.8	100	100	97	55	24	5	1	3600
66 (1)	275	"	21-2.2	5.7	98	98	94	49	18	4	1	3229
66 (2)	"	"	21-1.8	5.7	97	97	94	51	20	6	2	3189
67	"	"	21-2.2	7.6	98	98	94	49	18	4	1	3254
68 (1)	274	"	20-2.4	3.8	100	99	95	47	18	3	1	2856
68 (2)	"	"	19-2.0	3.8	100	99	96	51	19	4	1	3160
69	"	"	20-2.4	5.2	100	99	95	47	18	3	1	2928
70	275	"	21-2.2	5.7	98	98	94	49	18	4	1	3229
71	274	"	20-2.4	3.8	100	99	95	47	18	3	1	2856
72	"	"	20-2.4	2.3	100	99	95	47	18	3	1	2957
73	275	"	21-2.2	3.8	98	98	94	49	18	4	1	3123
74	"	"	27-2.7	5.7	100	99	76	35	13	3	1	2935
75	274	"	27-2.3	3.8	99	99	75	37	17	4	1	2532
76	280	Ball Mill	48-1.4	1.1	98	96	63	39	32	8	3	3353
77	"	"	48-1.4	4.8	98	96	63	39	32	8	3	3640
78	"	Vortec	27-2.1	1.1	98	98	79	45	21	4	1	3200
79	"	"	27-2.1	4.8	98	98	79	45	21	4	1	3346
80	"	"	27-2.4	1.1	99	99	77	39	16	4	1	2714
81	"	"	27-2.4	4.8	99	99	77	39	16	4	1	2928
82	14K2	Ball Mill	54-1.4	2.5	98	95	60	37	20	8	3	3563
83	"	"	54-1.4	5.6	98	95	60	37	20	8	3	3766
84	"	Vortec	27-2.1	2.5	100	100	79	45	22	4	1	3316
85	"	Vortec	27-2.1	5.6	100	100	79	45	22	4	1	3491
86	"	Vortec	27-2.2	2.5	99	99	76	39	16	4	1	2855
87	"	Vortec	27-2.2	5.6	99	99	76	39	16	4	1	3012

TABLE 7

SO₃ Content of Different Size-Fractions of a Cement*

Size Range	Percent of Whole	SO ₃ Content %	Percent of Total SO ₃
Whole	100	1.8	
0-7 micron	22	4.6	73
7-22	26	0.8	15
22-40	25	0.4	7.2
40-55	11	0.3	2.4
55	16	0.2	2.3

*Data from Swenson and Flint, NBS Journal 17 p. 263 1936

TABLE 8

Properties of 0.5 Water/cement Ratio Pastes Made from
Clinker 275 of 3472 cm²/gm Blended with Gypsum of
Three Different Finenesses

Percent Gypsum	$\bar{S}/A$	Gypsum BSS cm ² /g	Setting Time	Compressive Strengths (psi)		
				1 day	3 day	7 day
9.5	1.0	3530	4h 0m	900	2,600	5,000
"	"	5860	3h 58m	1,000	3,600	5,600
"	"	7830	3h 46m	1,050	4,000	6,000
7.6	0.8	3530	4h 0m	1,150	3,500	6,250
"	"	5860	4h 10m	1,250	3,350	5,800
"	"	7830	4h 0m	1,350	3,600	6,250
5.7	0.6	3530	4h 0m	930	2,900	5,500
"	"	5860	4h 0m	1,120	3,800	6,100
"	"	7830	4h 0m	1,140	3,500	6,150
3.8	0.4	3530	4h 4m	680	3,200	6,500
"	"	5860	4h 0m	650	3,100	6,300
"	"	7830	4h 10m	730	3,400	6,350
1.9	0.2	3530	6h 36m	220	2,700	6,350
"	"	5860	5h 25m	250	2,900	6,300
"	"	7830	5h 9m	250	2,800	6,500

*1-inch paste cubes

TABLE 9

Mini-Slump Pat Areas for 0.5 w/c
Pastes of Clinker 275 + 5.7% Gypsum

Nominal Size Range Microns	Pat Areas (in) ²	
	5856 cm ² /g Gypsum	7573 cm ² /g Gypsum
45-5	9.47	8.41
14-5	6.67	6.27*
45-2	3.97	3.04
20-2	2.75	2.09

*From Table 10, V17, 7835 cm²/g gypsum

TABLE 10

Effects of Pebble-Milling Time and Gypsum Fineness
on Blaine Values and Mini-Slump Pat Areas

Cement with 5856 cm ² /g T.A.				Cement with 7835 cm ² /g T.A.			
Cement	Time (min.)	Cement Blaine cm ² /g	Pat Area	Cement	Time (min.)	Cement Blaine cm ² /g	Pat Area
V16	15	2262	6.28	V17	15	2277	6.27
PMT1 (a)	2.5	2277	5.98				
"	5	2252	6.20	PMT2 (b)	5	2310	5.93
"	10	2278	5.34				
"	15	2264	5.82	"	15	2334	5.46
"	30	2277	5.73	"	30	2332	5.98
"	60	<u>2297</u>	<u>5.74</u>	"	60	<u>2354</u>	<u>5.68</u>
Mean Values		2280	5.87			2321	5.86

(a) 3,100 g charge with 1,550 g pebbles (nearly full mill)

(b) 1,500 g charge with 1,500 g pebbles

TABLE 11

Effect of Gypsum Fineness on Compressive Strength of
Hardened Cement Pastes
Clinker 275 w /c_o = 0.5

Series	Percent Gypsum	Gypsum BSS cm ² /g	Clinker BSS cm ² /g	Cement BSS cm ² /g	Compressive Strengths (psi)		
					1 day	7 days	28 days
I	3.8	3530	3472	3474*	680	6,500	-
	5.7	"	"	3475*	930	5,500	-
	7.6	"	"	3476*	1,150	6,250	-
I	3.8	5860	3472	3562*	650	6,300	-
	5.7	"	"	3608*	1,120	6,100	-
	7.6	"	"	3653*	1,250	5,800	-
I	3.8	7835	3472	3638*	730	6,350	-
	5.7	"	"	3721*	1,140	6,150	-
	7.6	"	"	3804*	1,350	6,250	-
II	3.8	7835	3645	3893	587	7,425	10,800
	5.7	"	"	4022	1,330	6,000?	10,950
	7.6	"	"	4108	1,600	7,400	9,775
III	5.7	11448	3390	3802	1,580	6,470	9,805
	7.6	"	"	3938	1,213	6,050	9,067
Inter-ground	5.7	12000 ^a	2880 ^b	3400	1,100	6,630	10,100
	7.6	"	2692 ^b	"	810	5,150	8,925

*Calculated from B.S.S. values of clinker and gypsum

^aAssumed

^bCalculated

TABLE 12

Series II Preliminary Paste Mixes of 0.5 w/c
Clinker 275 + 5.7% Gypsum^a

Cement	Nominal Particle Size Range (Microns)	Percent Finer than 5 microns	B.S.S. (cm ² /g)	Mini-Slump Area (in ²)	Bleeding (% Paste Volume)	Set Time	Compressive Strength (psi) (1" 0.5 w/c paste cubes)		
							1 Day	3 Days	7 Days
MB2	45-5	8	2183	9.47	19	5h 26m	630	2,600	4,550
MB3	14-5	4	2475	6.67	19	5h 10m	734	3,335	7,055
MB1	45-2	26	3534	3.97	3	5h 12m	1,296	3,500	6,620
MB4	20-2	35	3929	2.75	3	4h 51m	1,580	5,710	7,705
MB5	100-0	23	3600*	-	-	4h 0m	930	2,900	5,500
	(Ball-Milled)		3384**	10.8**		5h 0m	1,100	3,450	6,630

^aT.A.2, 5,856 cm²/g

*Calculated from clinker (3,472 cm²/g) and gypsum finenesses

**From a comparable mix with interground gypsum

TABLE 13

Blaine Finenesses and L.O.I. of Pebble-Milled Blends of
Clinker 275 and T.A. Gypsum of 7536 cm²/gm Blaine
Specific Surface (B.S.S)

Cement	Nominal Size Range (microns)	B.S.S. ⁺ (cm ² /g)	Percent Gypsum	L.O.I. (percent)	Clinker Size Fraction Percentages				Ball-Milled Grind 100-0 microns
					<45 microns	<20 microns	14-5 microns	8-1 microns	
PM1	45-2	3582	3.8	1.39	60	0	0	40	0
PM2	"	3624	5.7	1.78	60	0	0	40	0
PM3	"	3679	7.6	2.18	60	0	0	40	0
PM4	45-5	2224	3.8	1.25	80	0	20	0	0
PM5	"	2317	5.7	1.53	80	0	20	0	0
PM6	"	2409	7.6	1.97	80	0	20	0	0
PM7	14-5	2326	3.8	1.27	0	0	100	0	0
PM8	"	2390	5.8	1.67	0	0	100	0	0
PM9	"	2480	7.6	2.10	0	0	100	0	0
PM10	20-2	3577	3.8	1.57	0	55	0	45	0
PM11	"	3710	5.8	1.90	0	55	0	45	0
PM12	"	3751	7.6	2.32	0	55	0	45	0
PM13	100-0	3893	3.8	1.26	0	0	0	0	100
PM14	"	4022	5.8	1.85	0	0	0	0	100
PM15	"	4108	7.6	2.09	0	0	0	0	100

+Blaine values (cm²/g) for these blends without gypsum were: 3230 (45-2), 1988 (45-5),
 3494 (20-2), 2114 (14-5), and
 3645 (100-2)

TABLE 14

Blaine Finenesses and L.O.I. of Pebble-Milled Blends of
Clinker 274 Cement Clinker Size Fractions and T. A. Gypsum of
7835 cm²/g Blaine Specific Surface (B.S.S.)

Cement	Nominal Size Range (microns)	B.S.S. ⁺ cm ² /g	Gypsum Percent	L.O.I. Percent	Clinker Size Fraction Percentages				Ball-Milled Grind 100-0 Microns
					<45 Microns	<20 Microns	14-5 Microns	8-1 Microns	
PM 16	45-2	3295	2.32	1.13	65	0	0	35	0
PM 17	45-2	3316	3.78	1.40	65	0	0	35	0
PM 18	45-2	3456	5.20	1.68	65	0	0	35	0
PM 19	45-5	2106	2.32	0.96	80	0	20	0	0
PM 20	45-5	2158	3.78	1.27	80	0	20	0	0
PM 21	45-5	2239	5.20	1.53	80	0	20	0	0
PM 22	14-5	2265	2.32	1.01	0	0	100	0	0
PM 23	14-5	2310	3.78	1.32	0	0	100	0	0
PM 24	14-5	2382	5.20	1.60	0	0	100	0	0
PM 25	20-2	3601	2.32	1.17	0	55	0	45	0
PM 26	20-2	3671	3.78	1.47	0	55	0	45	0
PM 27	20-2	3710	5.20	1.72	0	55	0	45	0
PM 28	100-0	3620	2.32	1.26	0	0	0	0	100
PM 29	100-0	3655	3.78	1.55	0	0	0	0	100
PM 30	100-0	3753	5.20	1.82	0	0	0	0	100

⁺Blaine values (cm²/g) for these blends without gypsum were: 3160 (45-2), 2000 (45-5)
3540 (20-2), 2160 (14-5)
3486 (100-0)

TABLE 15

Properties of Cement Pastes Made From
Various Particle Size Ranges of Clinker 275

Cement - w/c			Nominal Size Range (Microns)	Gypsum Percent	B.S.S. cm ² /g	Pat Area in. ²	Time of Set. hrs:min.	Final w/c (Corrected for Bleeding)	1-inch Paste Cube Compressive Strength (psi)		
									1d	7d	28d
Clinker			45-2	0	3230	--	--	--	--	--	--
PM	1	0.35	45-2	3.8	3582	--	--	0.35	--	--	--
PM	1	0.50	45-2	3.8	3582	3.58	4:45	0.50	492	7,820	11,050*
PM	1	0.65	45-2	3.8	3582	8.17	7:45	0.57	110	3,930	5,850
PM	2	0.35	45-2	5.7	3624	--	2:22	0.35	4,897	11,510	14,975
PM	2	0.50	45-2	5.7	3624	3.02	4:15	0.45	1,500	6,665	9,200
PM	2	0.65	45-2	5.7	3624	7.89	5:30	0.53	700	4,067	6,100
PM	3	0.35	45-2	7.6	3679	--	2:50	0.35	5,752	12,900	16,400*
PM	3	0.50	45-2	7.6	3679	3.10	4:20	0.50	1,932	7,300	10,350
PM	3	0.65	45-2	7.6	3679	8.03	6:00	0.59	1,060	4,300	6,150*
Clinker			45-5	0	1988	--	--	--	--	--	--
PM	4	0.35	45-5	3.8	2224	--	3:30	0.35	1,612	12,250	14,450
PM	4	0.50	45-5	3.8	2224	9.03	5:30	0.39	622	7,600	12,050
PM	4	0.65	45-5	3.8	2224	17.56	6:15	0.48	273	4,125	6,950
PM	5	0.35	45-5	5.7	2317	--	3:30	0.30	1,760	13,650*	18,400
PM	5	0.50	45-5	5.7	2317	8.49	5:30	0.39	729	6,800	11,525
PM	5	0.65	45-5	5.7	2317	15.16	6:00	0.47	478	3,350	7,000

TABLE 15 (Continued)

Properties of Cement Pastes Made From
Various Particle Size Ranges of Clinker 275

Cement - w/c			Nominal Size Range (Microns)	Gypsum Percent	B.S.S. cm ² /g	Pat Area in. ²	Time of Set hrs:min.	Final w/c (Corrected for Bleeding)	1-inch Paste Cube Compressive Strength (psi)		
									1d	7d	28d
PM	6	0.35	45-5	7.6	2409	--	3:30	0.28	2,100	13,125*	17,050
PM	6	0.50	45-5	7.6	2409	7.91	5:45	0.40	680	5,450	10,700
PM	6	0.65	45-5	7.6	2409	14.75	6:58	0.46	417	3,200	6,850
Clinker			14-5	0	2114	--	--	--	--	--	--
PM	7	0.35	14-5	3.8	2326	--	--	0.35	--	--	--
PM	7	0.50	14-5	3.8	2326	4.89	5:30	0.43	710	9,500	10,850
PM	7	0.65	14-5	3.8	2326	11.58	6:00	0.48	365	5,175	6,760
PM	8	0.35	14-5	5.7	2390	--	3:25	0.34	3,250	12,250	15,110
PM	8	0.50	14-5	5.7	2390	4.28	5:16	0.45	777	8,600	10,675
PM	8	0.65	14-5	5.7	2390	11.66	6:15	0.51	458	5,050	7,010
PM	9	0.35	14-5	7.6	2480	--	3:30	0.34	3,600	17,100	18,725
PM	9	0.50	14-5	7.6	2480	5.43	5:30	0.40	952	9,450	14,450
PM	9	0.65	14-5	7.6	2480	12.49	6:45	0.46	545	4,800	7,150
Clinker			20-2	0	3494	--	--	--	--	--	--
PM	10	0.35	20-2	3.8	3577	--	--	0.35	--	--	--
PM	10	0.50	20-2	3.8	3577	2.00	4:50	0.50	482	9,425	10,825
PM	10	0.65	20-2	3.8	3577	5.47	8:50	0.65	512	4,500	5,000

TABLE 15 (Continued)

Properties of Cement Pastes Made From
Various Particle Size Ranges of Clinker 275

Cement -	w/c	Nominal Size Range (Microns)	Gypsum Percent	B.S.S. cm ² /g	Pat Area in. ²	Time of Set hrs:min.	Final w/c (Corrected for Bleeding)	1-inch Paste Cube Compressive Strength		
								1d	7d	28d
PM 11	0.35	20-2	5.7	3710	--	1:30	0.35	4,900	9,700	11,700
PM 11	0.50	20-2	5.7	3710	2.19	4:30	0.50	2,375	9,025	10,500
PM 11	0.65	20-2	5.7	3710	5.20	5:30	0.63	870	5,450	6,100
PM 12	0.35	20-2	7.6	3751	--	2:00	0.35	6,400	10,400	15,275
PM 12	0.50	20-2	7.6	3751	2.14	4:00	0.50	3,500	9,375	10,550
PM 12	0.65	20-2	7.6	3751	5.14	5:30	0.63	1,580	5,350	6,200
Clinker		100-0	0	3645	--	--	--	--	--	--
PM 13	0.35	100-0	3.8	3893	--	3:30	0.35	2,800	14,325	18,575
PM 13	0.50	100-0	3.8	3893	6.64	5:00	0.48	587	7,425	10,800
PM 13	0.65	100-0	3.8	3893	13.21	6:30	0.53	212	4,400	6,950
PM 14	0.35	100-0	5.7	4022	--	3:00	0.35	3,500	8,225?	16,025
PM 14	0.50	100-0	5.7	4022	6.03	4:45	0.47	1,330	6,000	10,950
PM 14	0.65	100-0	5.7	4022	13.65	6:15	0.51	567	3,550	6,300
PM 15	0.35	100-0	7.6	4108	--	3:00	0.35	5,125	12,775	16,800
PM 15	0.50	100-0	7.6	4108	5.73	5:00	0.45	1,600	7,400	9,775
PM 15	0.65	100-0	7.6	4108	12.58	6:30	0.55	527	3,725	5,975

*Highest value of 2 cubes (large variation).

? Both values suspected to be too low.

TABLE 16

Properties of Cement Pastes Made From
Various Particle Size Ranges of Clinker 274

Cement - w/c		Nominal Size Range (Microns)	Gypsum Percent	B.S.S. cm ² /g	Pat Area in. ²	Time of Set hrs:min.	Final w/c (Corrected for Bleeding)	1-inch Paste Cube Compressive Strength (psi)		
								1d	7d	28d
Clinker		45-2	0	3160*						
PM 16	0.35	45-2	2.32	3295	2.05	5:00	0.34	2,560	9,807	14,750
PM 16	0.50	45-2	2.32	3295	6.91	5:45	0.44	878	4,450	8,805
PM 16	0.65	45-2	2.32	3295	12.60	7:00	0.53	417	1,900	4,090
PM 17	0.35	45-2	3.78	3316	2.03	5:00	0.34	3,832	9,060	13,775
PM 17	0.50	45-2	3.78	3316	7.08	5:45	0.44	1,611	4,720	8,100
PM 17	0.65	45-2	3.78	3316	12.35	7:00	0.53	745	2,047	3,635
PM 18	0.35	45-2	5.20	3456	1.95	4:40	0.34	3,275	9,095	12,325
PM 18	0.50	45-2	5.20	3456	4.67	6:00	0.44	1,159	4,854	6,445
PM 18	0.65	45-2	5.20	3456	11.68	7:10	0.57	718	2,280	3,545
Clinker		45-5	0	2000*						
PM 19	0.35	45-5	2.32	2106	2.10	4:35	0.27	1,311	8,987	15,525
PM 19	0.50	45-5	2.32	2106	13.27	6:30	0.38	609	3,545	8,080
PM 19	0.65	45-5	2.32	2106	21.65	7:05	0.43	308	1,755	4,127
PM 20	0.35	45-5	3.78	2158	2.21	4:50	0.27	1,065	7,603	14,900
PM 20	0.50	45-5	3.78	2158	11.97	6:15	0.36	596	3,530	5,730
PM 20	0.65	45-5	3.78	2158	23.42	7:10	0.45	396	1,855	3,372

TABLE 16 (Continued)

Properties of Cement Pastes Made From
Various Particle Size Ranges of Clinker 274

Cement - w/c		Nominal Size Range (Microns)	Gypsum Percent	B.S.S. cm ² /g	Pat Area in. ²	Time of Set hrs:min.	Final w/c (Corrected for Bleeding)	1-inch Paste Cube Compressive Strength (psi)		
								1d	7d	28d
PM 21	0.35	45-5	5.2	2239	2.13	5:20	0.25	890	4,980	13,500
PM 21	0.50	45-5	5.2	2239	11.52	6:15	0.36	538	3,182	7,570
PM 21	0.65	45-5	5.2	2239	21.98	7:00	0.45	315	2,122	3,895
Clinker		14-5	0	2160*						
PM 22	0.35	14-5	2.32	2265	--	4:15	0.29	1,781	11,950	14,425
PM 22	0.50	14-5	2.32	2265	8.67	6:00	0.38	797	5,130	8,820
PM 22	0.65	14-5	2.32	2265	15.92	6:45	0.45	426	2,352	4,862
PM 23	0.35	14-5	3.78	2310	--	3:45	0.29	2,600	11,800	14,600
PM 23	0.50	14-5	3.78	2310	8.89	6:10	0.36	1,120	4,815	8,045
PM 23	0.65	14-5	3.78	2310	15.37	6:40	0.43	667	2,435	3,815
PM 24	0.35	14-5	5.20	2382	--	4:00	0.29	1,455	9,832	15,750
PM 24	0.50	14-5	5.20	2382	8.49	6:30	0.36	597	4,535	7,350
PM 24	0.65	14-5	5.20	2382	14.69	7:00	0.43	384	2,915	3,965
Clinker		20-2	0	3540*						
PM 25	0.35	20-2	2.32	3601	--	3:00	0.35	3,625	14,275	14,350
PM 25	0.50	20-2	2.32	3601	3.49	5:20	0.46	809	6,570	10,425
PM 25	0.65	20-2	2.32	3601	7.77	6:30	0.57	310	2,327	4,640

TABLE 16 (Continued)

Properties of Cement Pastes Made From
Various Particle Size Ranges of Clinker 274

Cement- w/c	Nominal Size Range (Microns)	Gypsum Percent	B.S.S. cm ² /g	Pat Area in. ²	Time of Set hrs:min.	Final w/c (Corrected for Bleeding)	1-inch Paste Cube Compressive Strength		
							1d	7d	28d
PM 26 0.35	20-2	3.78	3671	--	3:00	0.35	6,290	11,775	15,250
PM 26 0.50	20-2	3.78	3671	2.88	5:15	0.48	2,080	7,020	9,835
PM 26 0.65	20-2	3.78	3671	7.38	6:20	0.61	964	2,915	4,160
PM 27 0.35	20-2	5.20	3710	--	3:00	0.35	7,785	10,450	13,800
PM 27 0.50	20-2	5.20	3710	3.38	5:15	0.48	2,530	7,202	8,945
PM 27 0.65	20-2	5.20	3710	6.75	6:11	0.61	1,280	3,095	4,060
Clinker	100-0	0	3486						
PM 28 0.35	100-0	2.32	3620	2.99	4:45	0.33	2,056	9,045	14,100
PM 28 0.50	100-0	2.32	3620	9.76	6:10	0.44	589	2,755	5,870
PM 28 0.65	100-0	2.32	3620	19.38	7:20	0.51	214	1,292	2,868
PM 29 0.35	100-0	3.78	3655	2.77	5:00	0.33	3,160	9,775	14,625
PM 29 0.50	100-0	3.78	3655	9.12	6:20	0.44	1,175	4,022	6,563
PM 29 0.65	100-0	3.78	3655	20.02	7:20	0.51	515	1,855	3,180
PM 30 0.35	100-0	5.20	3753	2.81	4:50	0.35	2,385	9,875	13,475
PM 30 0.50	100-0	5.20	3753	8.89	7:00	0.44	955	4,355	6,370
PM 30 0.65	100-0	5.20	3753	18.98	7:38	0.51	525	2,290	3,645

*Estimated by extrapolation

TABLE 17

Pebble-Milled Blends of Clinker 274
Size Fractions and T.A. Gypsum
of 7835 cm²/g Blaine Specific Surface (B.S.S.)

Cement	Nominal Size Range (microns)	B.S.S. cm ² /g	Gypsum Percent	L.O.I. Percent	Clinker Size Fraction Percentages			
					<45 Microns	<20 Microns	14-5 Microns	8-1 Microns
PM 17	45-2	3316	3.78	1.40	65	0	0	35
PM 31	45-x	3084	3.78		75	0	0	25
PM 32	45-y	2686	3.78		85	0	0	15
PM 33	45-z	2533	3.78		90	0	0	10
PM 34	14-x	2930	3.78		0	0	75	25
PM 35	14-y	2687	3.78		0	0	85	15
PM 36	14-z	2561	3.78		0	0	90	10
PM 23	14-5	2310	3.78	1.32			100	0
PM 26	20-2	3671	3.78	1.47		55		45
PM 37	20-y	2970	3.78		0	85	0	15

TABLE 18

Properties of Cement Pastes Made From
Various Particle Size Ranges of Clinker 274
with 3.78% Gypsum

Cement - w/c			Nominal Size Range (Microns)	B.S.S. cm ² /g	Pat Area in. ²	Time of Set hrs:min.	Final w/c (Corrected for Bleeding)	1-inch Paste Cube Compressive Strength ^a (psi)		
								1d	7d	28d
PM 31	0.35		45-X	3084	2.32	4:46	0.34 ^b	3,636	10,070	12,647
PM 31	0.50		45-X	3084	8.08	5:55	0.44	1,424	4,492	7,606
PM 31	0.65		45-X	3084	13.24	7:05	0.53	885	2,596	4,127
PM 32	0.35		45-Y	2686	2.36	4:45	0.32	2,385	9,475	14,120
PM 32	0.50		45-Y	2686	9.83	6:09	0.41	1,010	4,232	7,006
PM 32	0.65		45-Y	2686	21.39	7:10	0.51	708	2,270	4,210
PM 33	0.35		45-Z	2533	2.32	5:00	0.32	1,661	9,175	12,912
PM 33	0.50		45-Z	2533	11.59	6:00	0.38	930	3,311	8,470
PM 33	0.65		45-Z	2533	22.25	7:28	0.45	580	3,183	5,957
PM 34	0.35		14-X	2930	--	3:35	0.32	4,507	11,795	14,851
PM 34	0.50		14-X	2930	5.50	5:40	0.41	1,727	5,749	10,222
PM 34	0.65		14-X	2930	10.27	6:15	0.51	1,131	3,381	5,315
PM 35	0.35		14-Y	2687	--	4:00	0.32	3,422	14,986	15,195
PM 35	0.50		14-Y	2687	6.40	6:11	0.40 ^b	1,886	6,376	11,395
PM 35	0.65		14-Y	2687	12.52	6:56	0.47	1,057	3,239	5,795

TABLE 18 (Continued)

**Properties of Cement Pastes Made From
Various Particle Size Ranges of Clinker 274
with 3.78% Gypsum**

Cement - w/c	Nominal Size Range (Microns)	B.S.S. cm ² /g	Pat Area in. ²	Time of Set hrs:min.	Final w/c (Corrected for Bleeding)	1-inch Paste Cube Compressive Strength ^a (psi)		
						1d	7d	28d
PM 36 0.35	14-Z	2561	--	3:55	0.32	3,332	11,311	12,615
PM 36 0.50	14-Z	2561	7.19	6:10	0.39 ^b	1,332	6,349	10,447
PM 36 0.65	14-Z	2561	14.15	7:20	0.45 ^b	937	3,072	5,719
PM 37 0.35	20-Y	2970	--	3:50	0.35	4,256	11,885	14,370
PM 37 0.50	20-Y	2970	5.60	6:00	0.44	1,837	5,840	11,210
PM 37 0.65	20-Y	2970	10.60	6:25	0.53	1,237	3,068	6,004

^aCalculated from 1x2-inch cylinder strengths.

^bEstimated by interpolation.

TABLE 19

**Series IIIa - Pebble-Milled Blends of 274 Cement Clinker Particle Size Fractions
and T.A. Gypsum of 11450 cm²/g Blaine Specific Surface (B.S.S.)**

Blend No.	Maximum Particle Size (microns)	Clinker Particle Size Fraction Percentage				B.S.S. of Clinker Blend*	Percent Gypsum	B.S.S. cm ² /g
		Ball-Milled Grind 3370 cm ² /g)	<30 Microns 2235 cm ² /g)	<20 Microns 2788 cm ² /g)	<8 Microns 4840 cm ² /g)			
PM 43	100	100	--	--	--	3370	3.78	3661
PM 64	30	0	85	0	15	2626	3.78	3160
PM 65	20	0	0	85	15	3096	3.78	3600

*Calculated from B.S.S. and percentages of particle size fractions.

TABLE 20

Mix Proportions and Properties of Concretes
made with Cements of Clinker 274 with 3.78% Gypsum

Cement	w/c	Cement Factor (bags/yd ³)	Slump (in.)	Aggre- gate (d)	% Fine Aggre- gate	Compressive Strength (psi)					
						Normal Mixing Time			Extended Mixing ^(e)		
						1d	7d	28d	1d	7d	28d
PM 43 (a)	0.45	6.1	2.9	E	29.6	1495	4645	6335	1875	5245	6120
PM 64 (b)	0.45	6.4	1.6	E	24.2	1695	5040	6725	2105	5860	7380
PM 65 (c)	0.45	7.2	2.1	E	25	2180	5600	6980	2360	6460	7460
PM 43	0.55	4.8	2.1	E	33	1165	3860	5115	1475	4895	5745
PM 64	0.55	4.8	2.3	E	29.3	930	2945	4100	1095	3345	4595
PM 65	0.55	5.3	3.2	E	33.9	1500	3725	4780	1395	3980	4725
PM 43	0.45	6.8	1.8	T	31.7	1960	5460	7395	2460	6495	8040
PM 64	0.45	8.6	2.0	T	22.0	2280	5180	7525	2480	6170	8750
PM 65	0.45	7.7	0.5	T	23.0	3115	6700	7945	3215	7500	8805

TABLE 20 (Continued)

Mix Proportions and Properties of Concretes
made with Cements of Clinker 274 with 3.78% Gypsum

Cement	w/c	Cement Factor (bags/yd ³)	Slump (in.)	Aggre- gate (d)	% Fine Aggre- gate	Compressive Strength (psi)					
						Normal Mixing Time			Extended Mixing ^(e)		
						1d	7d	28d	1d	7d	28d
PM 43	0.55	5.6	3.0	T	35.0	1090	3495	5125	1675	5215	6605
PM 64	0.55	6.1	2.5	T	27.9	1230	3845	5445	1885	5560	7115
PM 65	0.55	6.2	2.5	T	33.6	1965	5510	6835	2360	6555	7915

- (a) Ball-milled cement, 3,661 cm²/g
 (b) 30 micron maximum particle size, 3,160 cm²/g
 (c) 20 micron maximum particle size, 3,600 cm²/g
 (d) E is Elgin gravel; T is Thornton Limestone
 (e) 25 minutes of additional mixing

TABLE 21

Properties of Cement Pastes Made from Particle Size Controlled Cements

Clinker 275

Blend	Maximum Size Particles (microns)	Percent Fines Added	B.S.S. (a) cm ² /g	Percent (b) Gypsum	w/c (Original)	w/c (Corrected)	Work- ability (c)	Paste Cube Compressive Strength, psi					Extent of Hydration (d), Percent					Drying Shrinkage Percent	
								1d	7d	28d	28d (sealed)	60d	1d	7d	28d	28d sealed	60d	7d cured	28d cured
PM 38	100	-	3,002	5.7	0.4	0.386	W	2,875	10,400	14,750	13,100	15,050	35.0	68.2	82.8	73.6	84.1	0.272	0.323
PM 38	100	-	(3,390)	(0.6)	0.5	0.456	VW	1,580	6,470	9,805	-	-	-	-	-	-	-	0.335	0.430
PM 38	100	-	-	-	0.6	0.545	F	805	4,205	6,785	6,240	6,500	36.6	77.7	92.3	88.2	94.6	0.376	0.542
PM 39	100	-	3,938	7.6	0.4	0.389	W	2,602	9,580	14,862	-	-	-	35.0	68.3	79.7	-	0.241	0.333
PM 39	100	-	(3,390)	(0.8)	0.5	0.469	VW	1,213	6,050	9,067	-	-	-	-	-	-	-	0.255	0.375
PM 39	100	-	-	-	0.6	0.546	F	709	3,915	6,530	-	-	-	36.5	72.9	87.5	-	0.262	0.392
PM 44	30	10	3,329	5.7	0.4	0.390	S	2,637	10,422	14,950	12,500	17,650	36.2	77.0	87.6	79.6	89.3	0.294	0.321
PM 44	30	10	(2,755)	(0.6)	0.5	0.472	W	1,422	7,005	10,165	-	-	-	-	-	-	-	0.359	0.463
PM 44	30	10	-	-	0.6	0.548	F	865	4,955	7,310	7,100	7,250	37.8	79.7	93.4	93.2	96.4	0.366	0.503
PM 45	30	10	3,460	7.6	0.4	0.376	W	2,905	12,200	13,675	-	-	-	37.3	73.9	84.3	-	0.264	0.345
PM 45	30	10	(2,755)	(0.8)	0.5	0.454	VW	1,562	7,557	10,395	-	-	-	-	-	-	-	0.273	0.443
PM 45	30	10	-	-	0.6	0.546	F	900	4,940	6,980	-	-	-	40.3	79.8	93.7	-	0.272	0.431
PM 46	30	15	3,522	5.7	0.4	0.370	W	3,040	11,800	15,925	16,200	17,200	37.4	76.2	87.2	79.5	89.6	0.286	0.329
PM 46	30	15	(2,882)	(0.6)	0.5	0.452	VW	1,730	8,077	10,865	-	-	-	-	-	-	-	0.359	0.468
PM 46	30	15	-	-	0.6	0.545	F	900	4,950	7,230	7,310	7,325	39.3	81.0	95.9	93.2	96.2	0.406	0.604
PM 47	30	15	3,670	7.6	0.4	0.374	W	3,625	12,325	16,000	-	-	-	50.3	78.5	86.6	-	0.262	0.319
PM 47	30	15	(2,882)	(0.8)	0.5	0.464	VW	1,757	7,800	10,635	-	-	-	-	-	-	-	0.281	0.405
PM 47	30	15	-	-	0.6	0.542	F	1,190	4,890	6,430	-	-	-	52.8	84.2	94.0	-	0.287	0.490
PM 48	30	20	3,791	5.7	0.4	0.372	W	2,915	11,275	15,325	14,900	16,725	49.3	78.5	87.3	80.0	89.0	0.270	0.349
PM 48	30	20	(3,009)	(0.6)	0.5	0.448	VW	1,631	7,720	10,085	-	-	-	-	-	-	-	0.374	0.445
PM 48	30	20	-	-	0.6	0.544	F	936	4,655	6,315	7,150	7,300	49.2	85.2	96.0	94.0	97.0	0.434	0.572
PM 49	30	20	3,898	7.6	0.4	0.382	W	3,665	12,375	15,750	-	-	-	48.0	77.5	87.0	-	0.277	0.330
PM 49	30	20	(3,009)	(0.8)	0.5	0.469	VW	1,962	7,730	10,185	-	-	-	-	-	-	-	0.301	0.415
PM 49	30	20	-	-	0.6	0.535	F	1,112	5,287	6,990	-	-	-	51.7	82.2	94.8	-	0.309	0.466
PM 66	20	0	3,229	5.7	0.4	0.383	S	2,750	8,915	11,600	9,300	15,950	38.3	78.6	86.9	82.7	94.6	0.271	0.285
PM 66	20	0	(2,847)	(0.6)	0.5	0.457	W	1,728	8,945	9,060	-	-	-	-	-	-	-	0.359	0.453
PM 66	20	0	-	-	0.6	0.546	VW	994	5,560	6,870	5,710	7,675	39.5	84.8	93.3	94.8	100.0	0.399	0.583
PM 67	20	0	3,254	7.6	0.4	0.399	S	2,895	9,630	10,600	11,100	15,425	39.3	78.4	85.1	82.0	92.9	0.288	0.337
PM 67	20	0	(2,847)	(0.8)	0.5	0.469	W	1,726	8,335	9,115	-	-	-	-	-	-	-	0.300	0.455
PM 67	20	0	-	-	0.6	0.550	VW	1,055	5,555	6,905	6,990	7,525	40.8	84.7	91.9	93.6	99.7	0.316	0.501
PM 52	20	15	3,516	5.7	0.4	0.389	S	2,615	8,425	11,050	16,000	14,800	44.4	80.4	89.5	82.1	90.6	0.295	0.279
PM 52	20	15	(3,034)	(0.6)	0.5	0.450	W	1,599	8,605	9,395	-	-	-	-	-	-	-	0.388	0.418
PM 52	20	15	-	-	0.6	0.563	VW	954	5,665	6,965	7,710	6,825	45.9	86.2	95.5	93.9	97.1	0.462	0.584
PM 53	20	15	3,647	7.6	0.4	0.394	S	3,752	10,625	14,100	-	-	-	40.4	78.8	88.0	-	0.327	0.289
PM 53	20	15	(3,034)	(0.8)	0.5	0.458	W	2,297	7,480	9,845	-	-	-	-	-	-	-	0.341	0.405
PM 53	20	15	-	-	0.6	0.542	VW	1,250	4,925	6,990	-	-	-	43.8	85.8	94.5	-	0.350	0.465

(a) Numbers in parentheses are B.S.S. values for the ground clinker without gypsum.

(b) Numbers in parentheses are S/A = SO₃/Al₂O₃ mole ratios.

(c) VF = very fluid, F = fluid, VW = very workable, W = workable, S = stiff

(d) Calculated from w_n/c

TABLE 22

Properties of Cement Pastes Made from Particle Size Controlled Cements

Clinker 274

Cement	Maximum Size Particles (microns)	Percent Fines Added	B.S.S. (a) cm ² /g	Percent (b) Gypsum	w/c (Original)	w/c (Corrected)	Work- ability (c)	Paste Cube Compressive Strength, psi					Extent of Hydration (d), Percent					Drying Shrinkage Percent		
								1d	7d	28d	28d (sealed)	60d	1d	7d	28d	28d sealed	60d	7d cured	28d cured	
PM 40	100	-	3,566	3.78	0.4	0.359	W	2,577	7,845	13,138	-	10,400	13,500	41.1	66.8	81.5	73.1	83.9	0.271	0.327
PM 40	100	-	(3,370)	(0.6)	0.5	0.462	F	1,297	3,892	7,675	-	-	-	-	-	-	-	-	0.310	0.387
PM 40	100	-	-	-	0.6	0.539	VF	840	2,702	5,115	5,350	6,700	44.3	70.9	89.1	83.5	93.1	0.315	0.463	
PM 41	100	-	3,708	5.20	0.4	0.351	W	2,045	8,195	12,250	-	-	-	39.8	67.2	78.1	-	-	0.288	0.294
PM 41	100	-	(3,370)	(0.8)	0.5	0.440	F	1,087	4,780	7,285	-	-	-	-	-	-	-	-	0.319	0.337
PM 41	100	-	-	-	0.6	0.533	VF	623	2,685	4,945	-	-	-	42.1	71.9	85.8	-	-	0.336	0.371
PM 54	30	10	2,892	3.78	0.4	0.365	W	2,045	8,315	13,250	13,200	13,475	41.8	68.2	81.7	78.1	87.9	0.289	0.316	
PM 54	30	10	(2,522)	(0.6)	0.5	0.450	W	1,168	4,895	8,065	-	-	-	-	-	-	-	-	0.297	0.388
PM 54	30	10	-	-	0.6	0.531	F	836	3,158	5,760	5,670	5,630	4.57	73.9	88.7	88.4	95.3	0.315	0.403	
PM 55	30	10	3,042	5.20	0.4	0.381	W	1,608	8,730	13,875	-	-	-	40.4	68.2	81.8	-	-	0.337	0.358
PM 55	30	10	(2,522)	(0.8)	0.5	0.450	W	922	5,435	8,830	-	-	-	-	-	-	-	-	0.359	0.379
PM 55	30	10	-	-	0.6	0.531	F	616	3,552	5,445	-	-	-	44.1	74.4	87.7	-	-	0.344	0.388
PM 56	30	15	3,061	3.78	0.4	0.364	W	2,412	8,600	12,850	12,250	14,600	44.8	71.6	83.2	77.9	88.2	0.285	0.349	
PM 56	30	15	(2,617)	(0.6)	0.5	0.454	W	1,295	4,775	8,225	-	-	-	-	-	-	-	-	0.307	0.370
PM 56	30	15	-	-	0.6	0.530	F	840	3,315	5,580	5,340	5,185	48.6	75.3	89.6	88.3	97.0	0.330	0.442	
PM 57	30	15	3,241	5.20	0.4	0.373	W	1,888	9,125	14,125	-	-	-	42.2	72.0	81.8	-	-	0.303	0.321
PM 57	30	15	(2,617)	(0.8)	0.5	0.453	W	1,105	5,335	8,635	-	-	-	-	-	-	-	-	0.349	0.365
PM 57	30	15	-	-	0.6	0.540	F	723	3,950	5,420	-	-	-	47.2	77.6	89.7	-	-	0.336	0.371
PM 58	30	20	3,301	3.78	0.4	0.369	W	2,890	8,590	14,100	12,550	15,050	45.3	72.5	83.1	76.3	89.4	0.275	0.327	
PM 58	30	20	(2,712)	(0.6)	0.5	0.452	W	1,487	4,360	8,145	-	-	-	-	-	-	-	-	0.308	0.399
PM 58	30	20	-	-	0.6	0.530	F	999	3,315	5,595	6,020	5,115	48.4	77.5	90.2	87.1	98.0	0.320	0.451	
PM 59	30	20	3,345	5.20	0.4	0.381	W	2,210	8,860	14,350	-	-	-	42.7	72.0	82.3	-	-	0.290	0.330
PM 59	30	20	(2,712)	(0.8)	0.5	0.460	W	1,207	5,245	8,540	-	-	-	-	-	-	-	-	0.316	0.388
PM 59	30	20	-	-	0.6	0.546	F	820	3,480	5,405	-	-	-	48.0	78.3	88.7	-	-	0.318	0.411
PM 68	20	0	2,856	3.78	0.4	0.374	W	2,375	8,390	15,000	11,200	13,050	43.1	71.7	84.3	81.5	94.7	0.285	0.381	
PM 68	20	0	(2,788)	(0.6)	0.5	0.456	W	1,242	4,885	8,340	-	-	-	-	-	-	-	-	0.302	0.394
PM 68	20	0	-	-	0.6	0.532	F	850	3,005	5,985	5,410	6,675	46.6	77.8	90.0	90.3	98.3	0.306	0.460	
PM 69	20	0	2,928	5.20	0.4	0.375	W	1,690	9,645	15,550	12,050	17,475	39.7	70.9	82.8	80.2	92.9	0.323	0.373	
PM 69	20	0	(2,788)	(0.8)	0.5	0.461	W	1,105	5,835	9,240	-	-	-	-	-	-	-	-	0.353	0.405
PM 69	20	0	-	-	0.6	0.552	F	697	3,330	5,735	5,280	6,325	44.4	78.8	90.0	90.1	99.8	0.339	0.427	
PM 62	20	15	3,414	3.78	0.4	0.364	W	3,040	11,175	14,125	14,600	11,375	61.1	80.0	87.9	81.5	91.3	0.330	0.330	
PM 62	20	15	(3,004)	(0.6)	0.5	0.439	F	1,551	6,325	9,235	-	-	-	-	-	-	-	-	0.350	0.389
PM 62	20	15	-	-	0.6	0.520	VF	996	3,900	5,740	5,700	4,990	65.6	84.4	95.0	90.0	98.5	0.362	0.442	
PM 63	20	15	3,460	5.20	0.4	0.359	W	2,465	10,525	14,575	-	-	-	54.7	76.7	86.4	-	-	0.357	0.348
PM 63	20	15	(3,004)	(0.8)	0.5	0.450	W	1,236	6,265	8,450	-	-	-	-	-	-	-	-	0.382	0.383
PM 63	20	15	-	-	0.6	0.529	F	857	4,155	5,825	-	-	-	61.7	87.2	94.8	-	-	0.374	0.412

(a) Numbers in parentheses are B.S.S. values for the ground clinker without gypsum.

(b) Numbers in parentheses are S/A = SO₃/Al₂O₃ mole ratios.

(c) VF = very fluid, F = fluid, W = very workable, W = workable, S = stiff

(d) Calculated from w_n/c

TABLE 23

Compressive Strengths, f_c , and Gel-Space Ratios and $(G/S)^3$ Values Calculated from Original and
Non-Evaporable Water Contents of Hardened Cements made from Clinker 275

PM Cement	1 Day					7 Days				28 Days				60 Days			
	w _o /c	w _n /c	G/S	(G/S) ³	f _c (psi)	w _n /c	G/S	(G/S) ³	f _c (psi)	w _n /c	G/S	(G/S) ³	f _c (psi)	w _n /c	G/S	(G/S) ³	f _c (psi)
38	0.386	0.0839	0.503	0.127	2,875	0.1638	0.809	0.529	10,400	0.1988	0.911	0.756	14,750	0.2018	0.919	0.777	15,050
38	0.545	0.0877	0.396	0.062	805	0.1721	0.663	0.292	4,205	0.2216	0.787	0.487	6,785	0.2270	0.799	0.511	6,500
39	0.389	0.0839	0.500	0.125	2,602	0.1639	0.805	0.522	9,580	0.1912	0.886	0.696	14,862				
39	0.546	0.0875	0.394	0.061	709	0.1750	0.670	0.301	3,915	0.2100	0.759	0.437	6,530				
44	0.390	0.0868	0.512	0.135	2,637	0.1848	0.867	0.651	10,422	0.2102	0.936	0.819	14,950	0.2144	0.946	0.848	17,650
44	0.548	0.0907	0.405	0.066	865	0.1912	0.711	0.359	4,955	0.2241	0.790	0.493	7,310	0.2313	0.806	0.524	7,250
45	0.376	0.0896	0.540	0.158	2,905	0.1773	0.864	0.645	12,200	0.2023	0.935	0.817	13,675				
45	0.546	0.0968	0.420	0.079	900	0.1916	0.714	0.363	4,940	0.2249	0.794	0.500	6,980				
46	0.370	0.0898	0.548	0.164	3,040	0.1828	0.889	0.702	11,800	0.2094	0.962	0.891	15,925	0.2151	0.977	0.933	17,200
46	0.545	0.0942	0.420	0.074	900	0.1944	0.722	0.376	4,950	0.2301	0.806	0.524	7,230	0.2308	0.808	0.527	7,325
47	0.374	0.1208	0.674	0.306	3,625	0.1884	0.899	0.727	12,325	0.2079	0.953	0.864	16,000				
47	0.542	0.1267	0.532	0.151	1,190	0.2021	0.743	0.411	4,890	0.2257	0.799	0.510	6,430				
48	0.372	0.1183	0.667	0.296	2,915	0.1885	0.902	0.735	11,275	0.2096	0.960	0.885	15,325	0.2137	0.971	0.914	18,725
48	0.544	0.1181	0.503	0.127	936	0.2045	0.747	0.418	4,655	0.2304	0.808	0.527	6,315	0.2329	0.813	0.538	7,300
49	0.382	0.1153	0.643	0.265	3,665	0.1859	0.881	0.683	12,375	0.2088	0.943	0.840	15,750				
49	0.535	0.1240	0.529	0.148	1,112	0.1972	0.738	0.402	5,287	0.2274	0.810	0.531	6,990				

TABLE 23 (Continued)

Compressive Strengths, f_c , and Gel-Space Ratios and $(G/S)^3$ Values Calculated from Original and
Non-Evaporable Water Contents of Hardened Cements made from Clinker 275

PM Cement	1 Day					7 Days				28 Days				60 Days			
	w _O /c	w _n /c	G/S	(G/S) ³	f _c (psi)	w _n /c	G/S	(G/S) ³	f _c (psi)	w _n /c	G/S	(G/S) ³	f _c (psi)	w _n /c	G/S	(G/S) ³	f _c (psi)
66	0.383	0.0919	0.543	0.160	2,750	0.1887	0.887	0.699	8,915	0.2085	0.941	0.834	11,600				15,950
66	0.546	0.0948	0.421	0.075	994	0.2034	0.743	0.410	5,560	0.2239	0.791	0.495	6,870				7,675
67	0.399	0.0944	0.537	0.155	2,895	0.1881	0.864	0.645	9,630	0.2042	0.908	0.748	10,600				15,425
67	0.550	0.0978	0.429	0.079	1,055	0.2033	0.739	0.404	5,555	0.2206	0.780	0.475	6,905				7,525
52	0.389	0.1065	0.599	0.215	2,615	0.1930	0.891	0.707	8,425	0.2147	0.949	0.854	11,050	0.2175	0.956	0.874	14,800
52	0.563	0.1102	0.464	0.100	954	0.2068	0.709	0.356	5,665	0.2292	0.788	0.489	6,965	0.2330	0.796	0.5043	6,825
53	0.394	0.0969	0.553	0.169	3,752	0.1890	0.873	0.666	10,225	0.2112	0.933	0.812	14,100				
53	0.542	0.1052	0.460	0.098	1,250	0.2059	0.752	0.426	4,925	0.2268	0.812	0.515	6,990				

TABLE 24

Properties of Cement Pastes at Low and High Temperatures

Cement	Maximum Particle Size (microns)	Percent Fines Added	Percent A-140 Fines (d)	B.S.S. (a) cm ² /g	Percent Gypsum (b)	Work- ability (c) 42°F 100°F	Paste Cube Compressive Strength (psi)											
							4 Days			1 Day			7 Days			28 Days		
							42°F	73°F	100°F	42°F	73°F	100°F	42°F	73°F	100°F			
<u>Clinker 275 + Additions</u>																		
PM 42	100	-	0	3711 (3390)	5.7 (0.6)	F VW	1820	1146	3512	3200	6585	7740	6810	9215	7435			
PM 50	20	10	0	3485 (2916)	5.7 (0.6)	VW W	2160	1622	4485	4355	8565	9255	8365	9740	7595			
PM 51	20	10	0	3500 (2916)	7.6 (0.8)	- W	-	1921	4345	-	8160	7350	-	9120	11200			
PM 73	20	0	0	3123	3.8 (0.4)	VW -	1450	-	-	3245	-	-	8320	-	-			
PM 70	20	0	10	3229+ (2847)	5.7 (0.6)	VW W	2825	1504	4385	4600	7950	7405	8730	9810	10170			
<u>Clinker 274 + Additions</u>																		
PM 43	100	-	0	3661 (3370)	3.78 (0.6)	VF F	1526	1300	3270	2485	4500	6040	5745	7515	6470			
PM 64	30	15	0	3160 (2626)	3.78 (0.6)	F VW	1893	1539	3145	3270	5155	6205	7285	7020	7470			

TABLE 24 (Continued)

Properties of Cement Pastes at Low and High Temperatures

Cement	Maximum Particle Size (microns)	Percent Fines Added	Percent A-140 Fines (d)	B.S.S. (a) cm ² /g	Percent Gypsum (b)	Work-ability (c) 42°F 100°F	Paste Cube Compressive Strength (psi)									
							4 Days	1 Day			7 Days			28 Days		
							42°F	73°F	100°F	42°F	73°F	100°F	42°F	73°F	100°F	
<u>Clinker 274 + Additions (Continued)</u>																
PM 60	20	10	0	3369 (2932)	3.78 (0.6)	VW VW	2108	1588	4015	3535	6135	7150	6830	7040	7710	
PM 61	20	10	0	3402 (2932)	5.2 (0.8)	- VW	-	-	3920	-	-	8025	-	-	6845	
PM 72	20	0	0	2957	2.32 (0.4)	F -	2286	-	-	3615	-	-	8420	-	-	
PM 71	20	0	10	2856+ (2788)	3.78 (0.6)	VW VW	2655	2127	3245	4310	5825	5530	7225	8385	7100	

(a) Numbers in parentheses are values for the ground clinker without gypsum

(b) Numbers in parentheses are B/A = SO₃/Al₂O₃ mole ratios

(c) VF = very fluid, F = fluid, VW = very workable, W = workable

(d) A-140 is ground Iowa limestone; this is the less than 6 micron fraction, 12992 cm²/g

TABLE 25

Properties of Cement Pastes made with the High-Alkali
and High-Sulfate Clinkers
0.5 Water-Cement Ratio

Cement	Maximum Particle Size (Microns)	Percent Fines Added	Percent Gypsum (a)	L.O.I. %	B.S.S. (cm ² /g)	w/c Corrected	Work Ability	Mini Slump Pat Area	Time of Set hr:min.	Compressive Strength (psi)		
										1d	7d	28d
280 Cements												
PM76	100	-	1.06 (0.4)	0.54	3353	0.429	F	9.24	5:00	690	6,270	9,535
PM76-77	"	-	2.92 (0.6)	-	3497	0.454	F	8.60	5:00	1,401	5,685	8,775
PM77	"	-	4.79 (0.8)	-	3640	0.431	F	9.57	5:00	1,755	5,540	6,995
PM78	30	15	1.06 (0.4)	0.81	3200	0.468	VW	4.85	3:30	755	6,375	8,365
PM78-79	"	"	2.92 (0.6)	-	3273	0.456	W	4.82	4:10	1,549	6,285	8,710
PM79	"	"	4.79 (0.8)	-	3346	0.451	VW	4.99	4:15	2,350	6,280	8,970
PM80	30	5	1.06 (0.4)	0.65	2714	0.471	VW	6.26	3:30	620	7,060	10,130
PM80-81	"	"	2.92 (0.6)	-	2821	0.439	VW	5.64	4:12	1,366	6,305	8,240
PM81	"	"	4.79 (0.8)	-	2928	0.452	VW	5.72	4:00	1,830	6,380	9,270

TABLE 25 (Continued)

Properties of Cement Pastes made with the High-Alkali
and High-Sulfate Clinkers
0.5 Water-Cement Ratio

Cement	Maximum Particle Size (Microns)	Percent Fines Added	Percent Gypsum (a)	L.O.I. %	B.S.S. (cm ² /g)	w/c Corrected	Work Ability	Mini Slump Pat Area	Time of Set hr:min.	Compressive Strength (psi)		
										1d	7d	28d
<u>14K2 Cements</u>												
PM82	100	-	2.48 (0.4)	1.85	3563	0.455	F	11.20	7:05	301	4,295	7,600
PM82-83		-	4.05 (0.6)	-	3665	0.452	F	10.78	6:20	890	4,755	7,980
PM83	"	-	5.61 (0.8)	-	3766	0.466	F	9.84	7:10	1,023	4,520	6,350
PM84	30	15	2.48 (0.4)	1.74	3316	0.463	VW	7.39	5:40	397	5,100	9,210
PM84-85	"	"	4.05 (0.6)	-	3404	0.467	VW	6.90	5:12	1,109	4,150	7,825
PM85	"	"	5.61 (0.8)	-	3491	0.471	VW	6.57	5:50	1,330	4,840	7,740
PM86	30	5	2.48 (0.4)	1.70	2855	0.450	F	8.61	6:00	406	4,630	9,060
PM86-87	"	"	4.05 (0.6)	-	2934	0.460	F	8.43	5:18	949	4,025	7,625
PM87	3	"	5.61 (0.8)	-	3012	0.459	VW	7.33	6:05	710	4,210	7,195

(a) Sulfate to aluminate mole ratios are given in parentheses.