

269
3/14/80

DR-923

ENERGY

COO-4269-2

MASTER

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

Progress Report, November 1978—January 1979

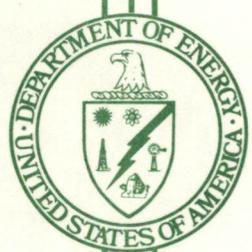
By
R. A. Helmuth

March 1979

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

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

NOI-HAKUHOZOO



U. S. DEPARTMENT OF ENERGY

Division of Industrial Energy Conservation

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

"This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy \$7.00
Microfiche \$3.50

Report to

DEPARTMENT OF ENERGY
Washington, D.C.
ERDA Contract No. EC-77-C-02-4269
PCA Contract No. CR-7523-4330

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

Progress Report
November-December 1978, January 1979

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, or completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Submitted by

R. A. Helmuth

CONSTRUCTION TECHNOLOGY LABORATORIES
A Division of the Portland Cement Association
5420 Old Orchard Road
Skokie, Illinois 60077

March 1979

Progress Report - November, December 1978, January 1979
Phase I Energy Conservation Potential of
Portland Cement Particle Size Distribution Control
DOE (ERDA) Contract No.: EC-77-C-02-4269
PCA Contract No.: CR 7523-4330

R. A. Helmuth
Portland Cement Association
Skokie, Illinois

SUMMARY

The preliminary concrete tests (Series IIIa) were completed. It was found that more experience will be required with the proportioning of concretes made with the particle size controlled cements to optimize the performance of such concretes. Nevertheless, workable mixes and better strengths were obtained with cements of much lower cement clinker finenesses than with normally ground cements. This conclusion was more definitely confirmed by ASTM C109 mortar tests, in which the proportions were held constant. Mortar flow tests showed the particle size controlled cement mortars also had better flow characteristics.

Almost all of the work on the effects of particle size ranges on strength and drying shrinkage (Series IIIb) was completed. The main conclusions we have reached are:

1. 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.
2. Some of these particle size controlled cements produce as high (and often much higher) strengths at all ages

- from 1 to 60 days at Blaine finenesses substantially lower (450 to 800 cm²/g) than the normal grinds of the same composition.
3. The less than 30 micron cements have Blaine finenesses about 450 cm²/g less than the normally ground cements for equal 1 day strengths. The less than 20 micron cements have Blaine finenesses 700 to 800 cm²/g less than the controls for equal 1 day strengths.
 4. The superior strength development of these particle size controlled cements is due to the more rapid and more complete hydration of the cement.
 5. The optimum gypsum content for strength of the particle size controlled cements is higher than that of the normally ground cements.
 6. For all of the cements, the drying shrinkage increased with the water-cement ratio and curing time, or degree of hydration.
 7. 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.
 8. 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.

9. 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 true; particle size controlled cements seem to be able to tolerate higher sulfate contents without loss of strength.
10. The optimum gypsum content for strength agrees better with that for drying shrinkage for the particle size controlled cements than for normally ground cements.

The work on the effects of mixing and curing temperature (Series IV) was also nearly completed. Tests at 42°F and 100°F showed that the particle size controlled cements usually yielded considerably higher strengths than the normally ground cements at equal ages. The exceptions were cases where the sulfate (or carbonate additions) were deliberately high or low. Additions of 10% ground limestone improved 1 and 28 day strengths, despite the facts that 10% of the cement was replaced with limestone and the water-cement ratios were higher; the mixes were made at equal (0.5) water-solids ratios.

The work on the effects of high alkali and high sulfate clinker cements (Series V) was begun.

Additional blends are being prepared with ground limestone additions for tests at room temperature to obtain paste flow properties, strength, and shrinkage data for these cements.

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.

The preparation of the cements for Series IIIa was described in detail in the August-September-October 1978 Quarterly Report. Two particle size controlled cements were prepared from the low C_3A content clinker MCC-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 Table I of the last Quarterly Report.

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)	3,661	101
PM 64 (30 microns maximum)	3,160	114
PM 65 (20 microns maximum)	3,600	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 on p. 6 of the May-June-July 1978 Report. The mortar strength tests showed that their strength development is 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 properties, slumps, and strength data for these concretes are given in Table I. 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 I. 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 properly optimize 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.

Series IIIb - Effects of Particle Size Ranges on Strength and Drying Shrinkage

The Series IIIb 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 IIIb tests are given in Tables II and III. The preparation of most of the cements used was described in detail in the August-September-October Quarterly Report. Table II contains the results for the high C_3A content cements made with clinker MCC-275; Table III contains the data for the low C_3A content cements using clinker MCC-274. As noted in the letter report for December 1978 (page 3), we decided to replace four of the cements (PM 50, 51, 60, 61) with four others (PM 66, 67, 68, 69) of lower fines contents and lower B.S.S. values. 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.

As noted in the Series IIIa discussion, 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 (see p. 2 in the last Quarterly Report), B.S.S. values for both the finished cements and the ground clinker without gypsum are given for each cement. 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:

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

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/cm³ 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 C₃A cements bled slightly more than the high C₃A 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 II and III 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 MCC-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 MCC-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 MCC-275. Hence, the stiffness of the MCC-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 $-79^{\circ}C$ (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 for each cement clinker plus gypsum 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. Figures 1 and 2 show such results for the MCC-275 and MCC-274 cements. For the high C₃A clinker MCC-275, Fig. 1 shows 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 (as drawn) because the cement is completely hydrated. Hence, we used the value of 0.240 as the value for the completely hydrated MCC-275 cements. Plots for two water-cement ratios are given for the ball-milled cements to show the retarding effect of the dense hydrates formed in low water-cement ratio pastes on the hydration of the remaining cement.

Similar results for the MCC-274 (low C₃A) cements are given in Fig. 2. 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 III.

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, the strength data are plotted in Figs. 3 to 10 vs. the water-cement ratio, corrected for bleeding. 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 have better strengths at \bar{S}/A of 0.8. In a few cases, the less than 20 micron MCC-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 Figs. 3 to 10 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	MCC-275 (12% C_3A)		MCC-275 (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

The Blaine finenesses of the less than 20 micron MCC-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. 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. For the 20 micron maximum size, the required Blaine finenesses are $700\text{-}800 \text{ cm}^2/\text{g}$ lower than the controls.

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 leads 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 con-

trol, we have calculated the gel-space ratio, G/S, for each hardened paste for which the degree of hydration was determined.

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 do 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 MCC-275) is:

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

These calculated values are given in Table IV. 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 MCC-275 ball-milled 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. 11. 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:

$$f_{co} = 19,400 \text{ psi at } w_o/c = 0.4$$

$$f_{co} = 14,000 \text{ psi at } w_o/c = 0.6$$

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.

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. 11.

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. 11. 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 the MCC-275 cements are plotted in Figs. 12 to 19. In each of these figures, the straight lines for the ball-milled controls are also shown for comparison. For some of these high C_3A cements, those in Fig. 12 for the <30 micron cements at $\bar{S}/A = 0.6$ at w/c = 0.4, the <20 micron cements at $\bar{S}/A = 0.6$ and 0.8 at w/c = 0.4 (Figs. 14 and 18), the strengths are significantly less than that of the ball-milled controls. This implies that in these 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. We believe this is mainly because of the restrictions imposed on the particle size distributions because of 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 (0.12 inch) 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 II and III 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. Further work is required to optimize these effects.

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 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.

Series IV - 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 (MCC-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 pebble milled blends PM 50, 51, 60, and 61 originally prepared for but not used in Series IIIb were used here. They 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 V. The Blaine finenesses of the particle size controlled cements were 200-500 cm²/g less than the particle size controlled 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 12,992 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 V, we have also included for comparison compressive strength data from other test series at 73°F. Not all of these pastes have been tested so the data at 73°F is not complete. 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.

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 $42^{\circ}F$, and the 7 day strengths of PM 51, PM 70, and PM 71 at $100^{\circ}F$. These three had high sulfate or carbonate additives. 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 would 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.

Series V - Effects of High-Alkali and High Sulfate Clinkers

The pebble milled blends of the high sulfate-high alkali clinker cement have been completed and paste mixes were begun on February 1.

The high alkali cement clinker blends were also completed and mixes began on February 6. Additional blends are being prepared with limestone additions for tests at room temperature to obtain paste flow properties, strength, and shrinkage data for these cements.

Concluding Discussion

To obtain even greater improvements in the utilization of the cement for strength, we believe it will be necessary to introduce other variables into the cement clinker-gypsum-water systems to reduce the water requirement for flow. Our earlier work has shown that wider particle size distributions have lower water requirements. We think this is because the amount of interstitial water between the water films on the cement particles increases as the particle size distribution is made narrower, and that this water does not contribute to flow. We do not want to broaden the cement particle size distributions because the larger particles never hydrate completely, and the fines not only add to the water requirement, but also form high porosity regions that lower the strength. In addition, the early hydration of the fines can also cause premature stiffening.

It is not necessary that the coarse or very fine particles required to broaden the size distribution be made of cement

clinker. We can just as well use additions of ground limestone, quartz, slags, or fly ash of the required particle sizes. These additions will reduce the sizes of the interstitial water pockets and make the hardened paste structure more uniform as far as dense gel formation is concerned. Relatively inert solid materials will not cause abnormal setting and will remain as hard inclusions to increase the strength and decrease drying shrinkage. We also found that the flow properties of finely ground limestone are much better than that of cements and finely ground quartz (p. 17, February-April-May 1978 Report), and so may be used to replace cement fines and reduce the water requirement. Calcium carbonate (limestone) also reacts slowly to produce calcium carboaluminates. These tend to stabilize the ettringite formed by the reaction between the gypsum and the aluminates so that the ettringite does not revert to the mono-sulfate form. All of these effects should tend to increase strengths and reduce drying shrinkage. Hence, we are beginning to explore the potential of such additions to the particle size controlled cements to more efficiently utilize the cement. In addition, the replacement of cement clinker with these materials has great potential for energy conservation and should also increase the capacity of cement plants. If 20% of the cement can be replaced by such inert materials, 20% of the kiln fuel can be saved and the capacity of the industry also be similarly increased.

Another way to improve the flow properties of these particle size controlled cements and permit their use at much lower water-cement ratios is by the use of water-reducing admixtures.

These organic admixtures disperse the cement particles in the water and prevent the normal single floc structure formation in the fresh pastes by neutralizing surface charges. Such dispersed cements flow much more freely than normal cement-water pastes. Such fresh paste structures are much closer to the simple model of fresh pastes described in the proposal for this work and should permit greater exploitation of these ideas with respect to the formation of hardened paste structures that more efficiently utilize the cement for strength development and drying shrinkage reduction.

We hope to examine the use of both the powdered mineral additions and water-reducing admixtures with the particle size controlled cements in the next phase of this investigation. We are just starting to prepare a proposal for this next Phase II, and hope to submit it shortly after the final report on this Phase I.

TABLE I

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 I (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 II

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 Gypsum (b)	w/c (Original)	w/c (Corrected)	Workability (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	0.583
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	18,725	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	78.0	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 III

Properties of Cement Pastes Made from Particle Size Controlled Cements

Clinker 274

Blend	Maximum Size Particles (microns)	Percent Finest Added	B.S.S. (a) cm ² /g	Percent Gypsum (b)	w/c (Original)	w/c (Corrected)	Workability (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	VW	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	2,605	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	VW	1,168	4,095	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	86.4	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	VW	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	VW	1,295	4,775	8,225	-	-	-	-	-	-	-	0.307	0.370
PM 56	30	15	-	-	0.6	0.530	F	840	3,315	5,580	5,540	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	VW	1,105	5,535	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	VW	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	14,550	-	-	42.7	72.0	82.3	-	-	0.290	0.330
PM 59	30	20	(2,712)	(0.8)	0.5	0.460	VW	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	VW	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	VW	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	VW	3,040	11,175	14,125	14,600	11,375	61.1	80.0	87.8	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	VW	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, VW = very workable, W = workable, S = stiff

(d) Calculated from w_n/c

TABLE IV

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 Blend	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	
29	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	
2016	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	0.428	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 IV (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 Blend	1 Day					7 Days				28 Days				60 Days			
	w_o/c	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 V

Properties of Cement Pastes at Low and High Temperatures

Blend	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	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	7435				
PM 50	20	10	0	3485 (2916)	5.7 (0.6)	VW W	2160	1622	4485	4355	8565	9255	8365	7595				
PM 51	20	10	0	3500 (2916)	7.6 (0.8)	- W	-	1921	4345	-	8160	7350	-	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	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	6470				
PM 64	30	15	0	3160 (2626)	3.78 (0.6)	F VW	1893	1539	3145	3270	5155	6205	7285	7470				

31

2016

TABLE V (Continued)

Properties of Cement Pastes at Low and High Temperatures

Blend	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	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	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	7100				

(a) Numbers in parentheses are 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

(d) A-140 is ground Iowa limestone; this is the less than 6 micron fraction, 12,992 cm²/g

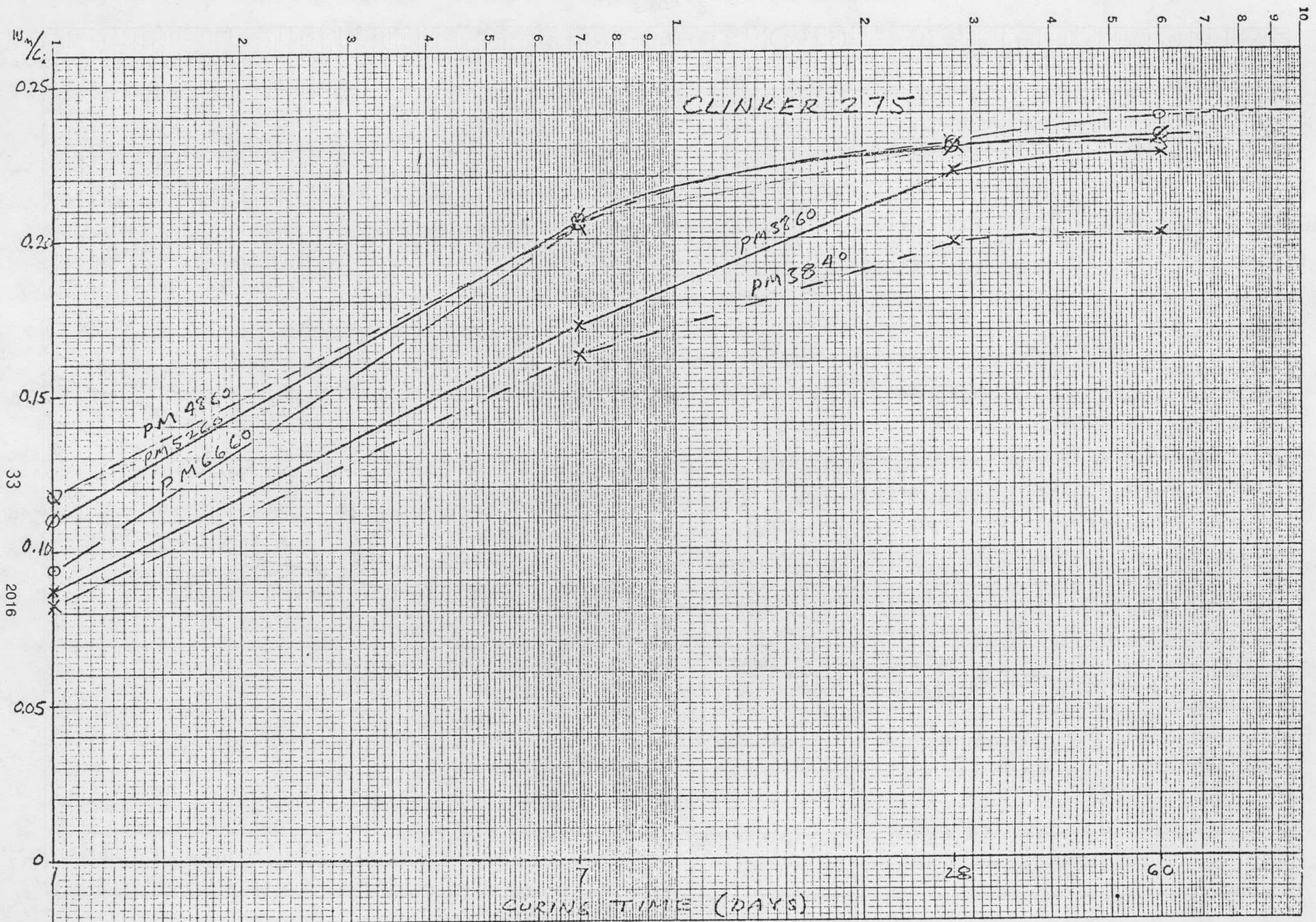


Fig. 1

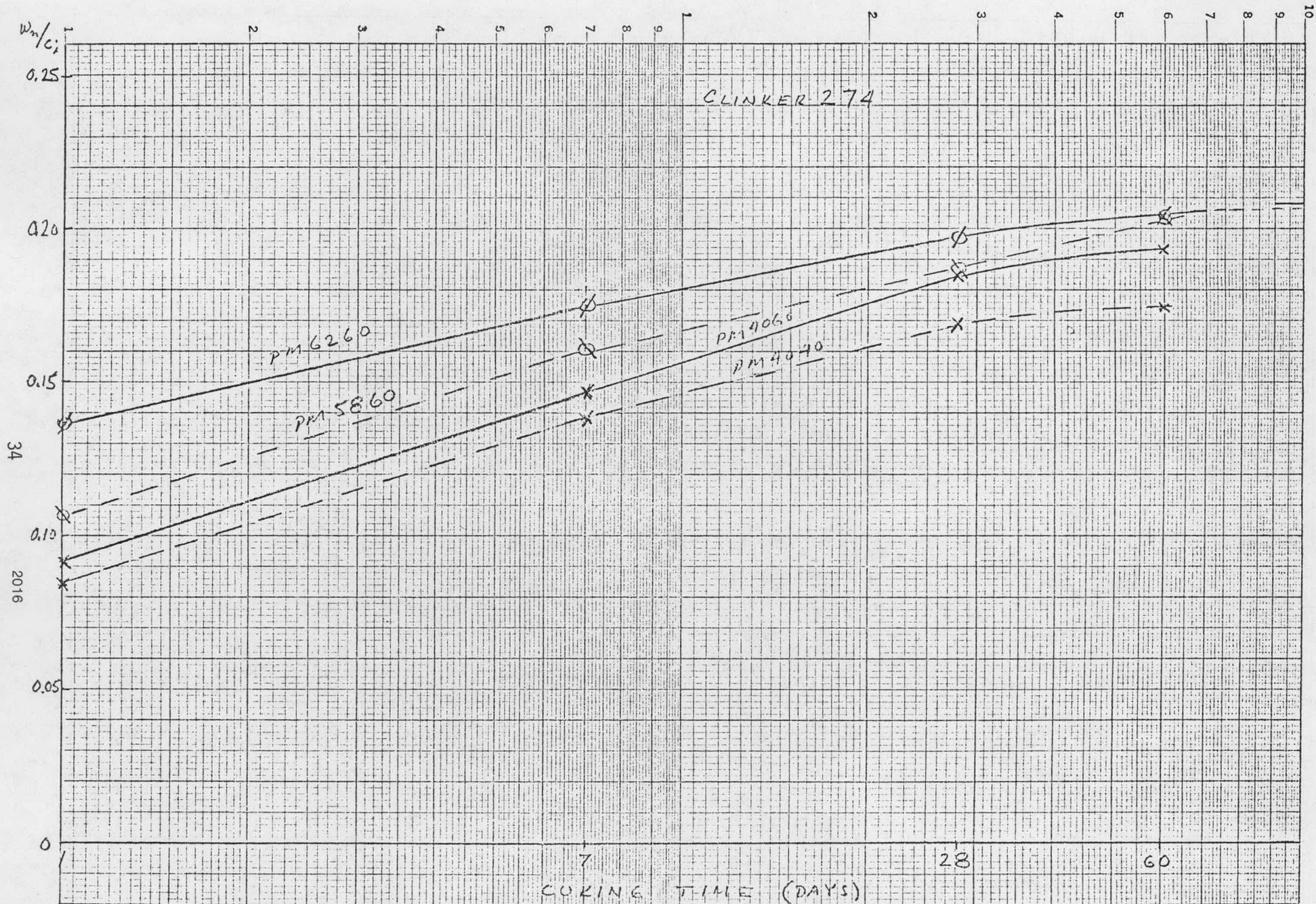


Fig. 2

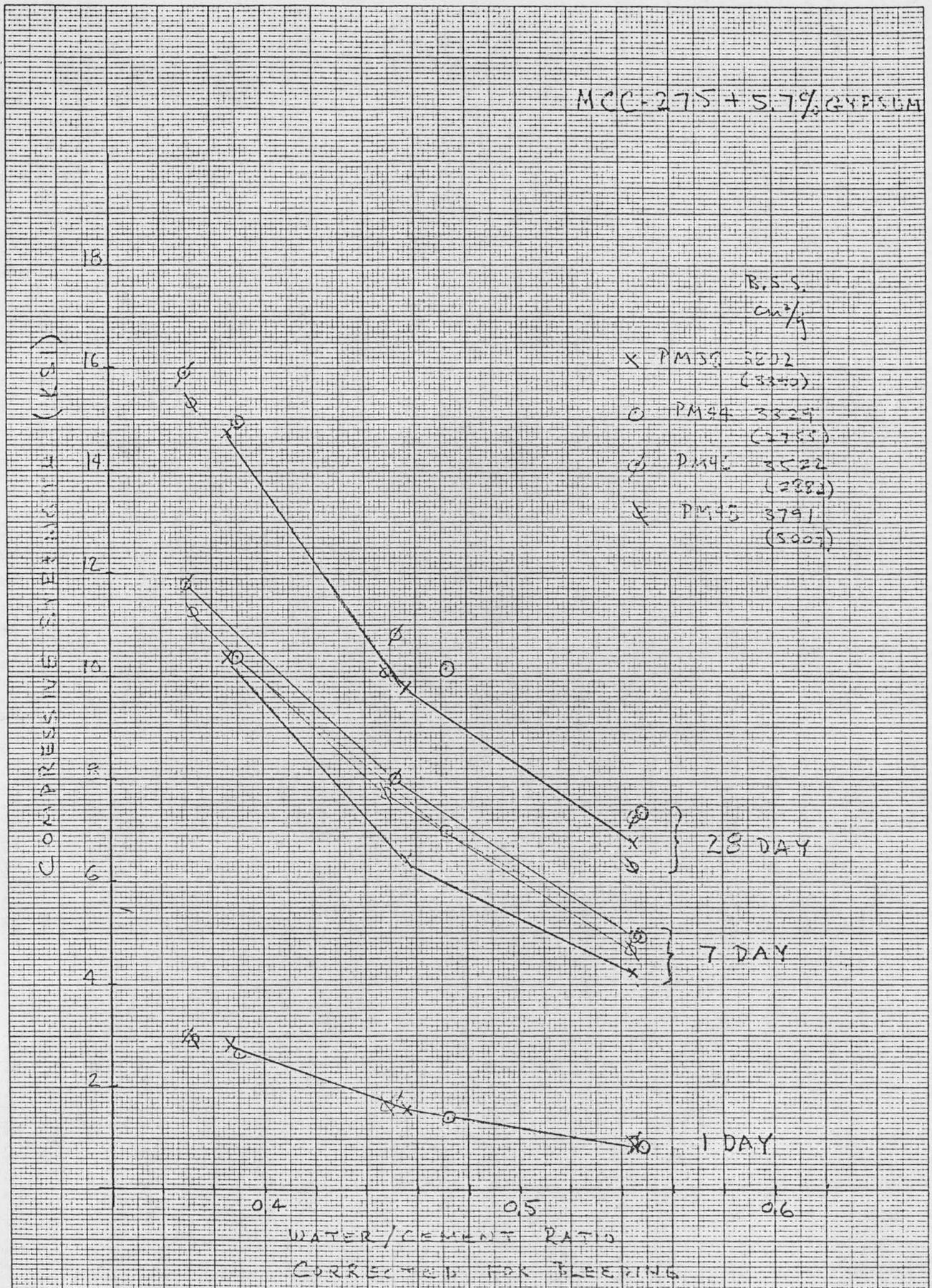


Fig. 3

MCC-275 + 5.7% GYPSUM

COMPRESSIVE STRENGTH (KSI)

B.S.S.
Unit/g

- x PM 58 3202 (3843)
- o PM 66 3229 (2847)
- ∅ 2M52 3516 (3084)

18

16

14

12

10

8

6

4

2

28 DAY

7 DAY

1 DAY

0.4

0.5

0.6

WATER/CEMENT RATIO
CORRECTED FOR BLEEDING

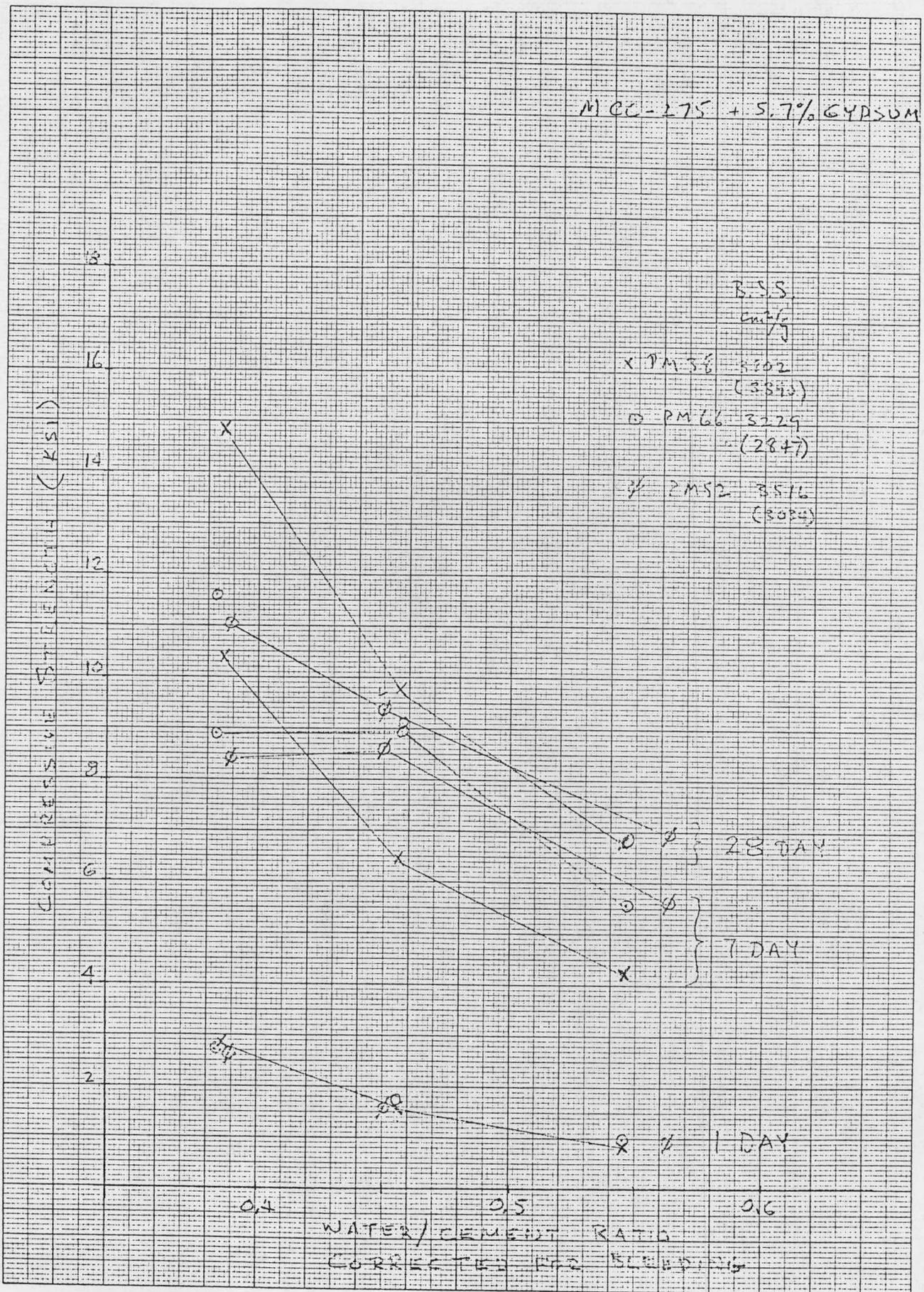


Fig. 4

MCC-275 + 7.6% GYPSUM
 < 30 MICRON CEMENTS

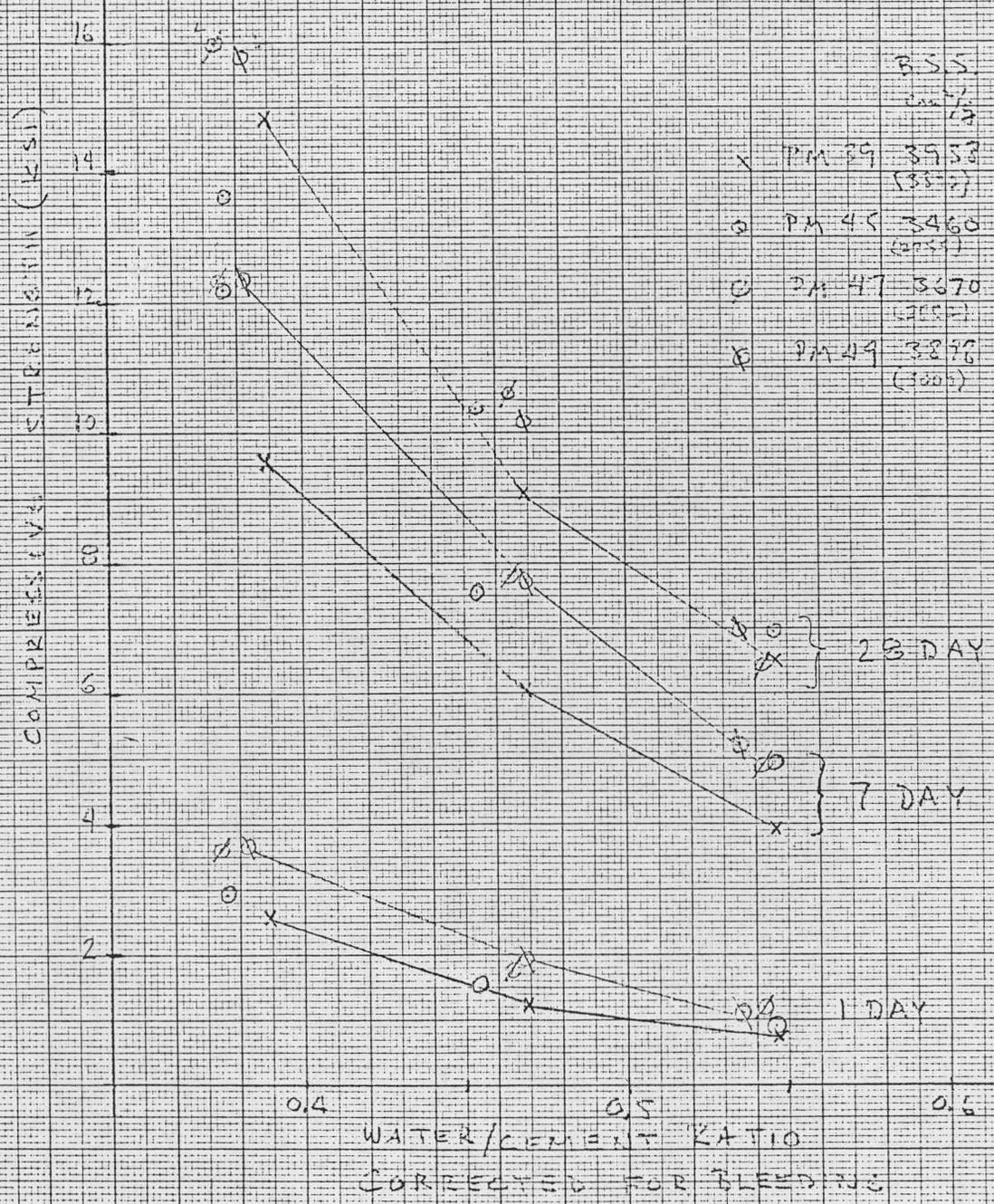


Fig. 5
 37

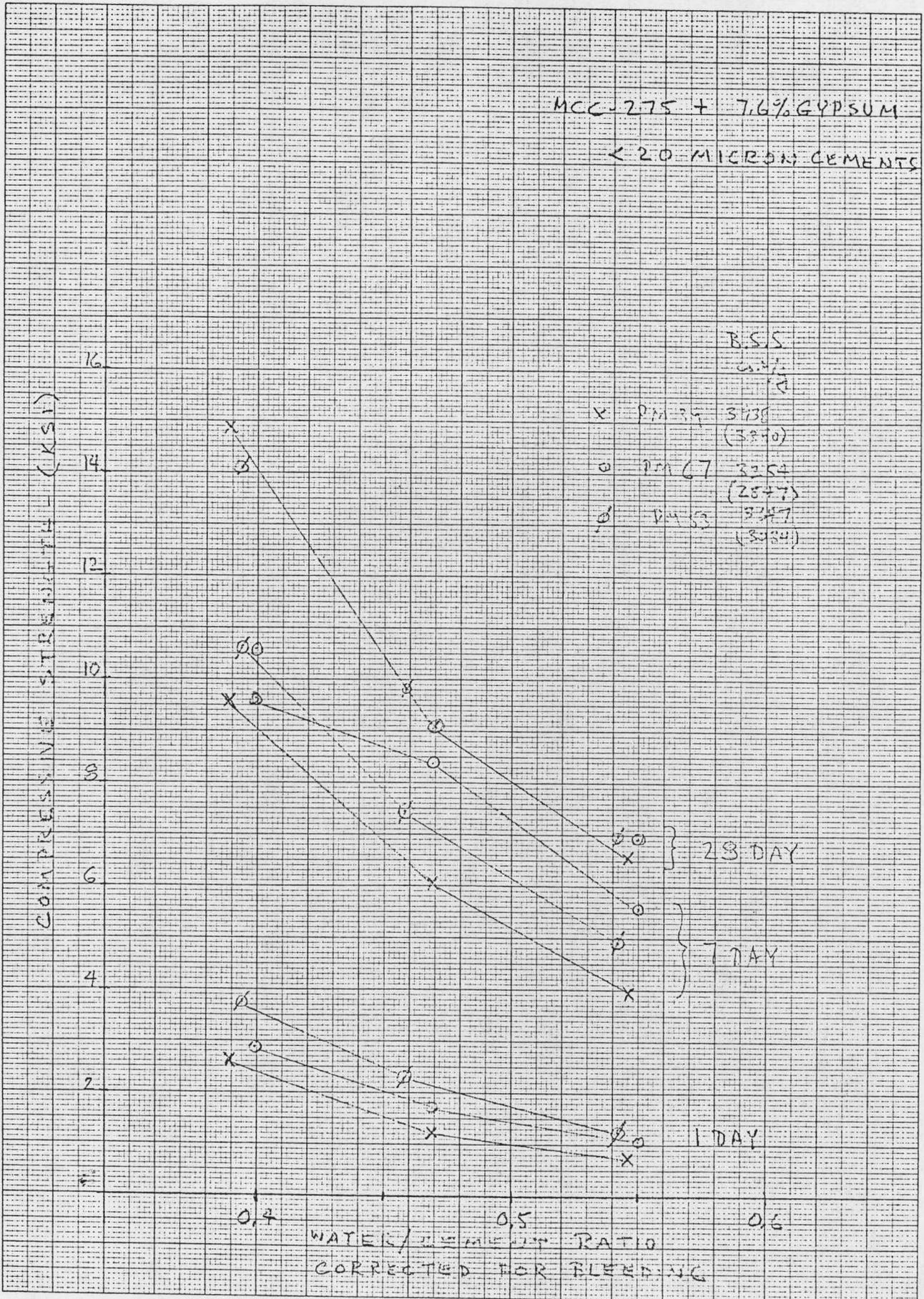


Fig. 6

MCC-274 + 3.73% GYPSUM

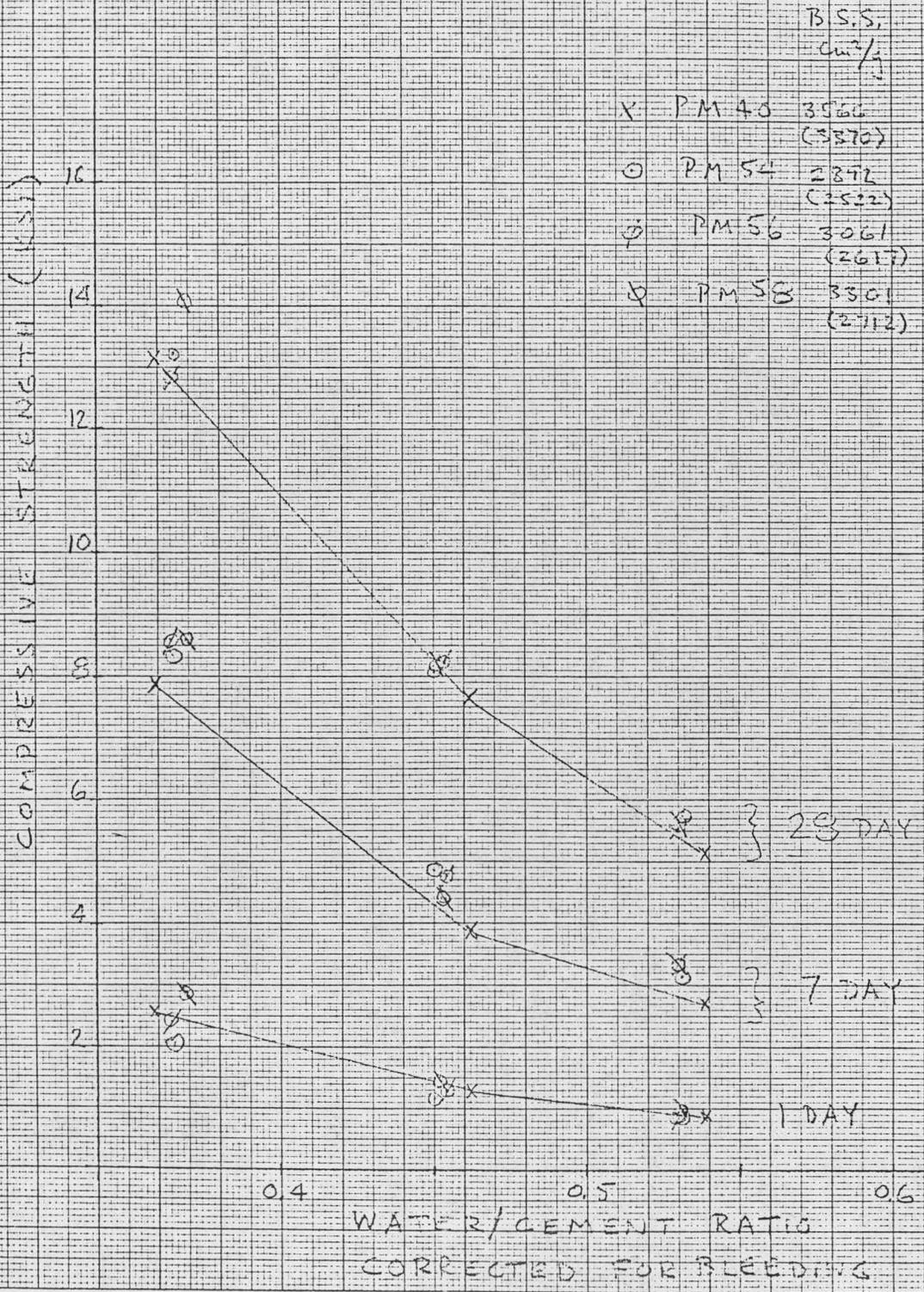


Fig. 7

MCC 2.74 + 5.2% GYPSUM

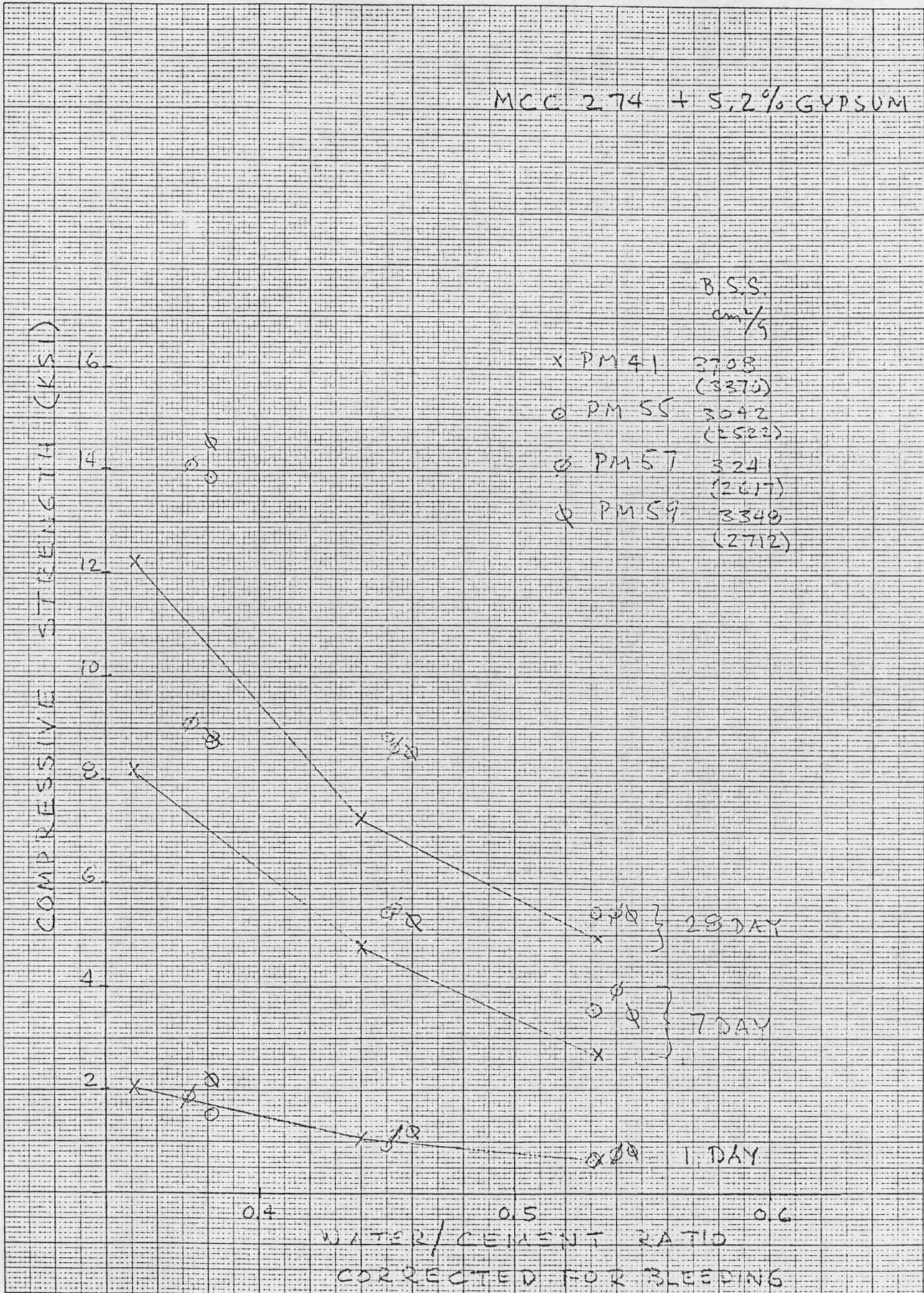


Fig. 9

MCC 274 + 3.78% GYPSUM

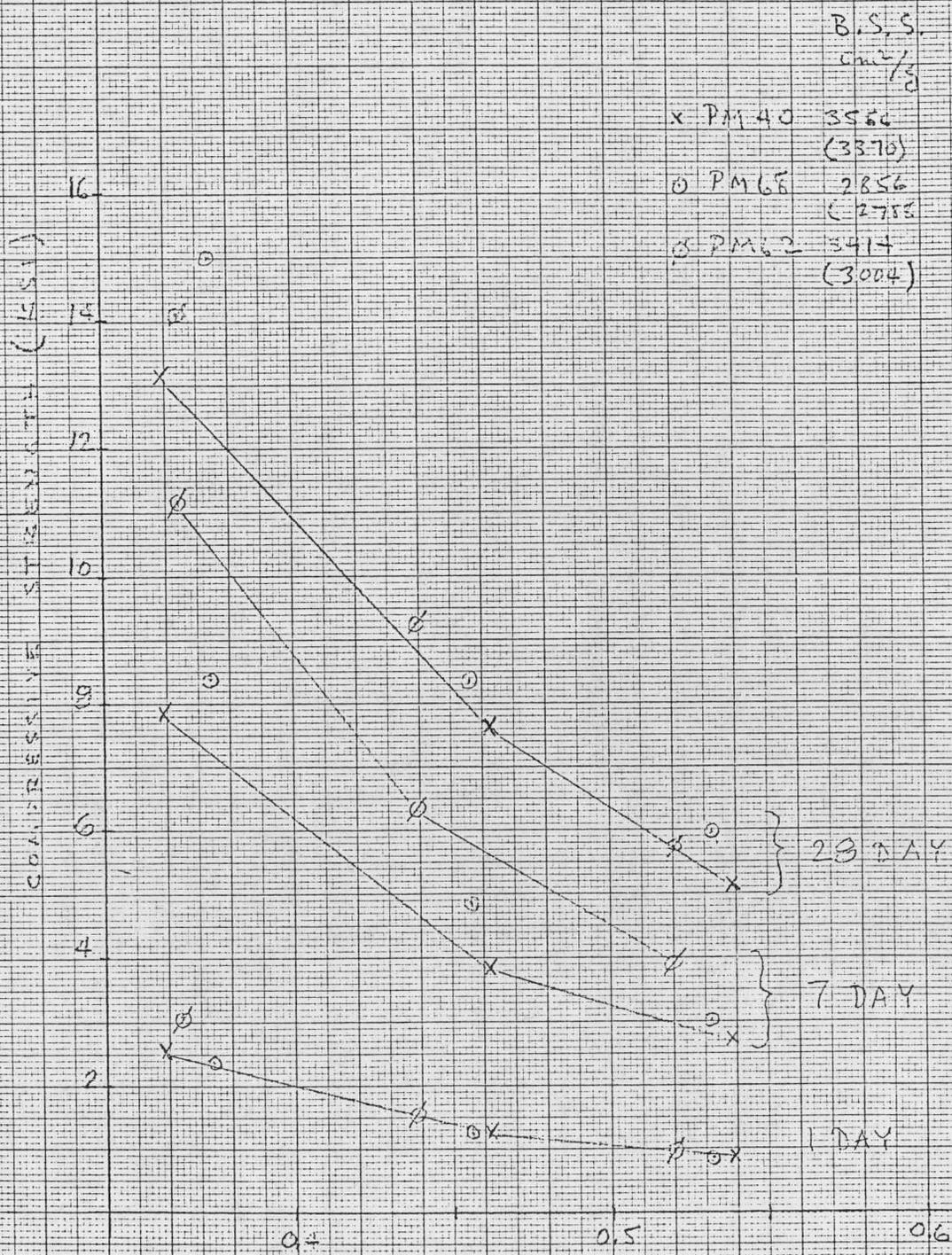


Fig. 8
41

MCC 274 + 5.2% GYPSUM

< 20 MICRON CEMENTS

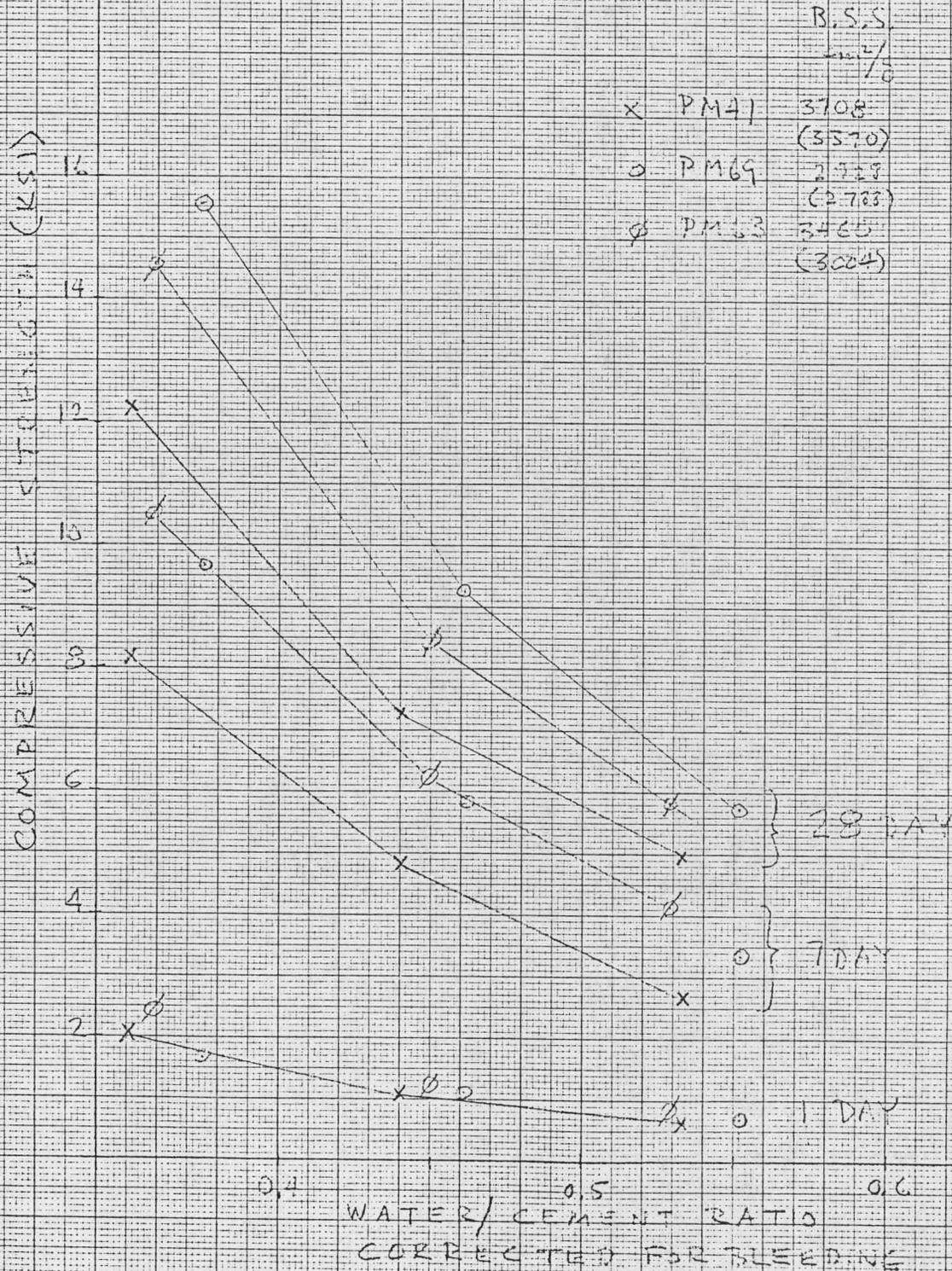


Fig. 10

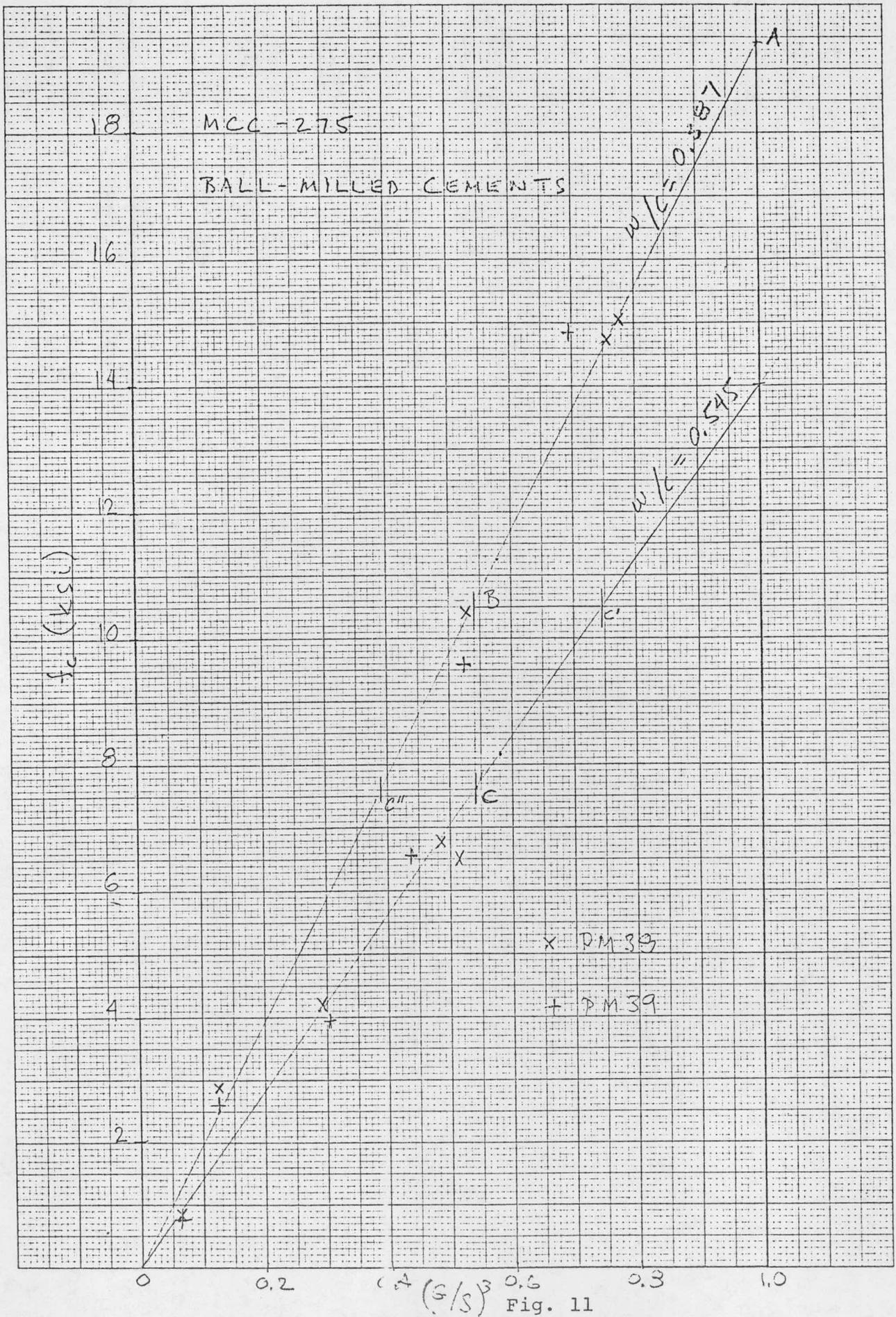


Fig. 11

MCC-275 + 5.7% GYPSUM

18 < 30 MICRONS $w/c = 0.4$

$S/A = 0.6$

f_c (KSI)

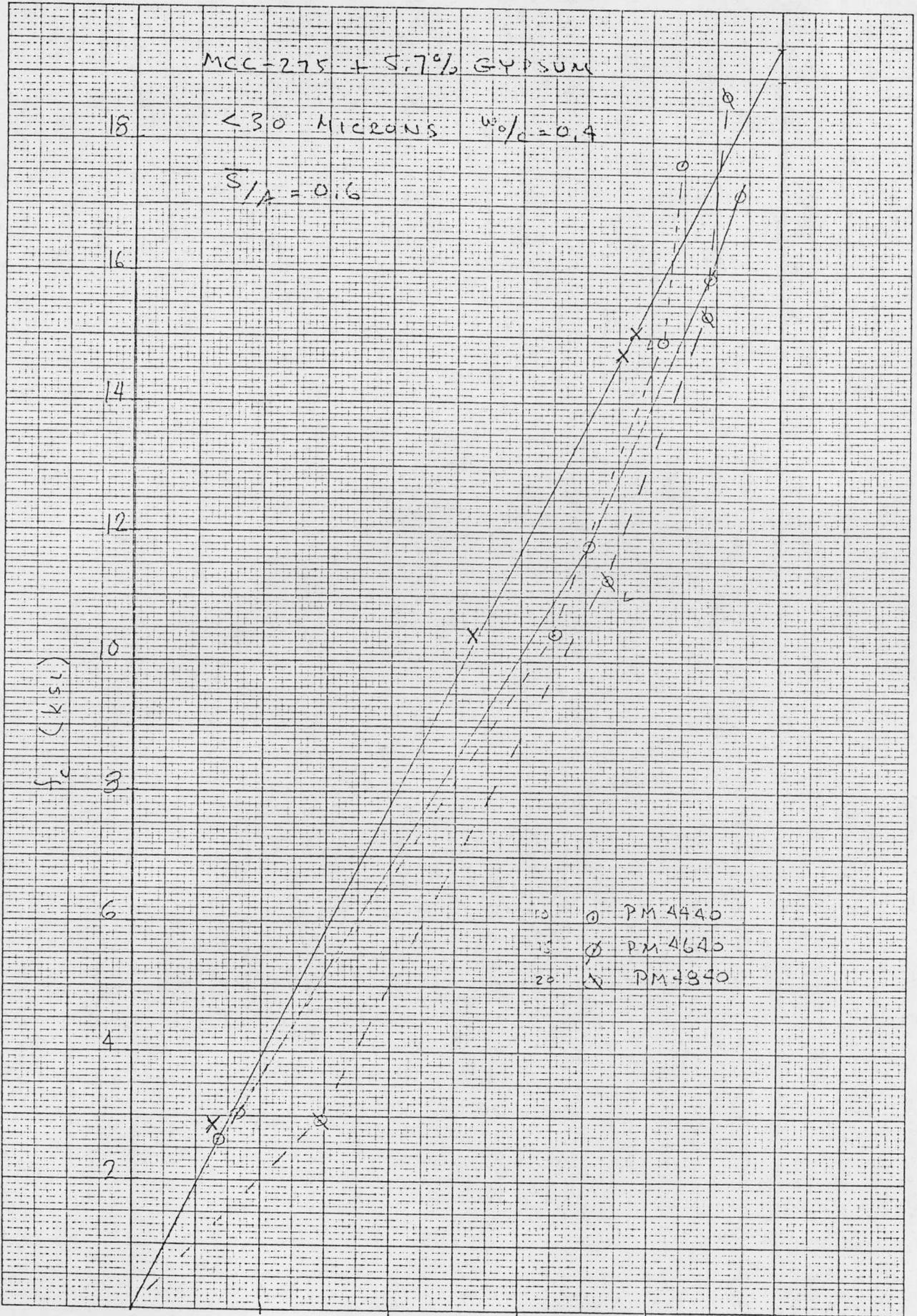
18
16
14
12
10
8
6
4
2

0 0.2 0.4 0.6 0.8 1.0

$(g/s) 13$

- 10 ○ PM 4440
- 15 ○ PM 4640
- 20 X PM 4840

44 Fig. 12



MCC-275 + 5.7% GYPSUM

18 < 30 MICRONS $w/c = 0.6$

$S/A = 0.6$

f_c (KSI)

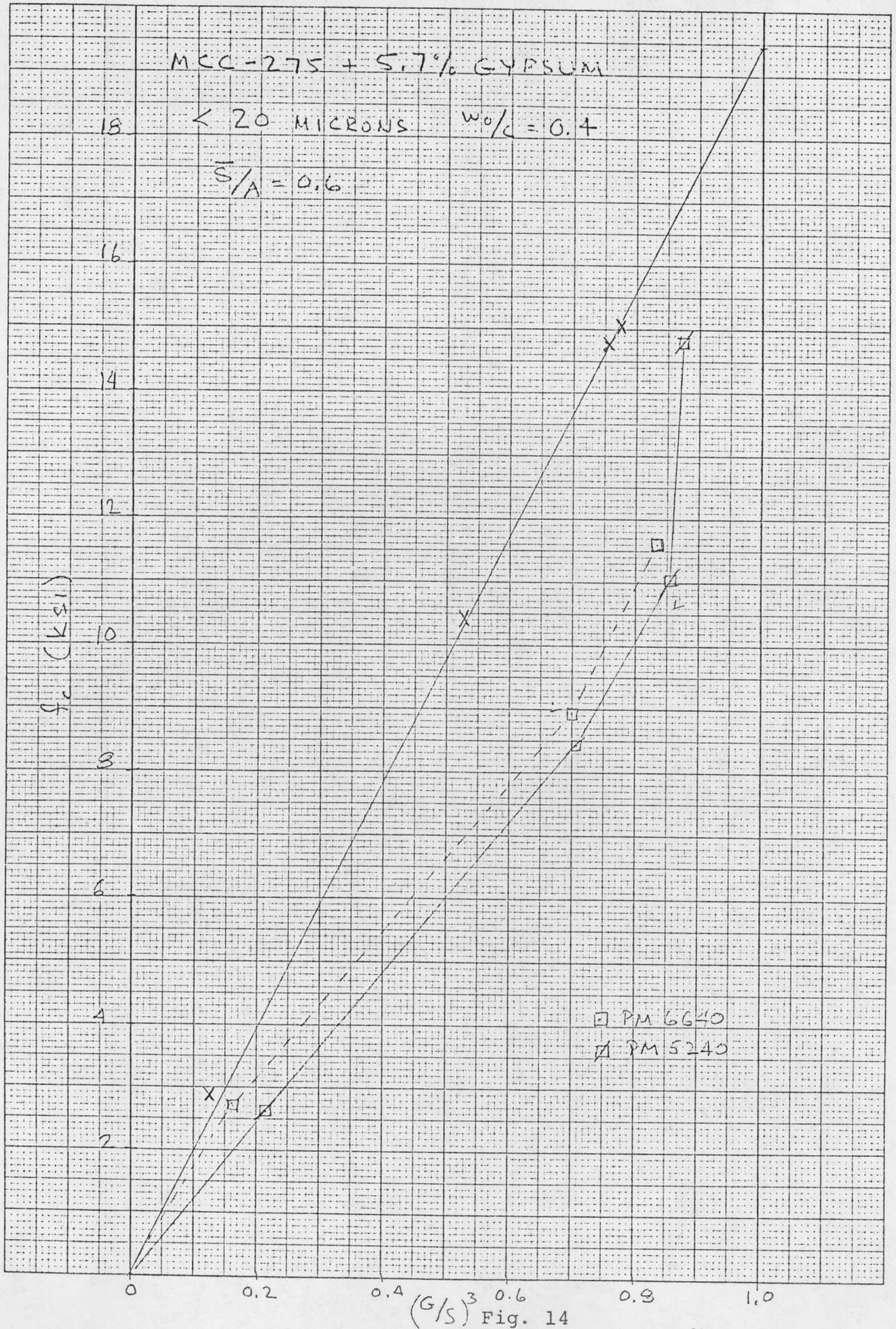
18
16
14
12
10
8
6
4
2

$(GEL/SPACE)^3$ Fig. 13

- PM4460
- ◊ PM4660
- ⊗ PM4860

2016





MCC-275 + 5.7% GYPSUM

13

< 20 MICRONS $w_0/c = 0.6$

$S/A = 0.6$

16

14

12

f'_c (KSI)

10

8

6

4

2

0

0.2

0.4

$(G/S)^3$

Fig. 15

0.6

0.8

1.0

□ PM6660

▣ PM5260

MCC-275 + 7.6% GYPSUM
 < 50 MICRONS $w/c = 0.4$
 $S/A = 0.8$

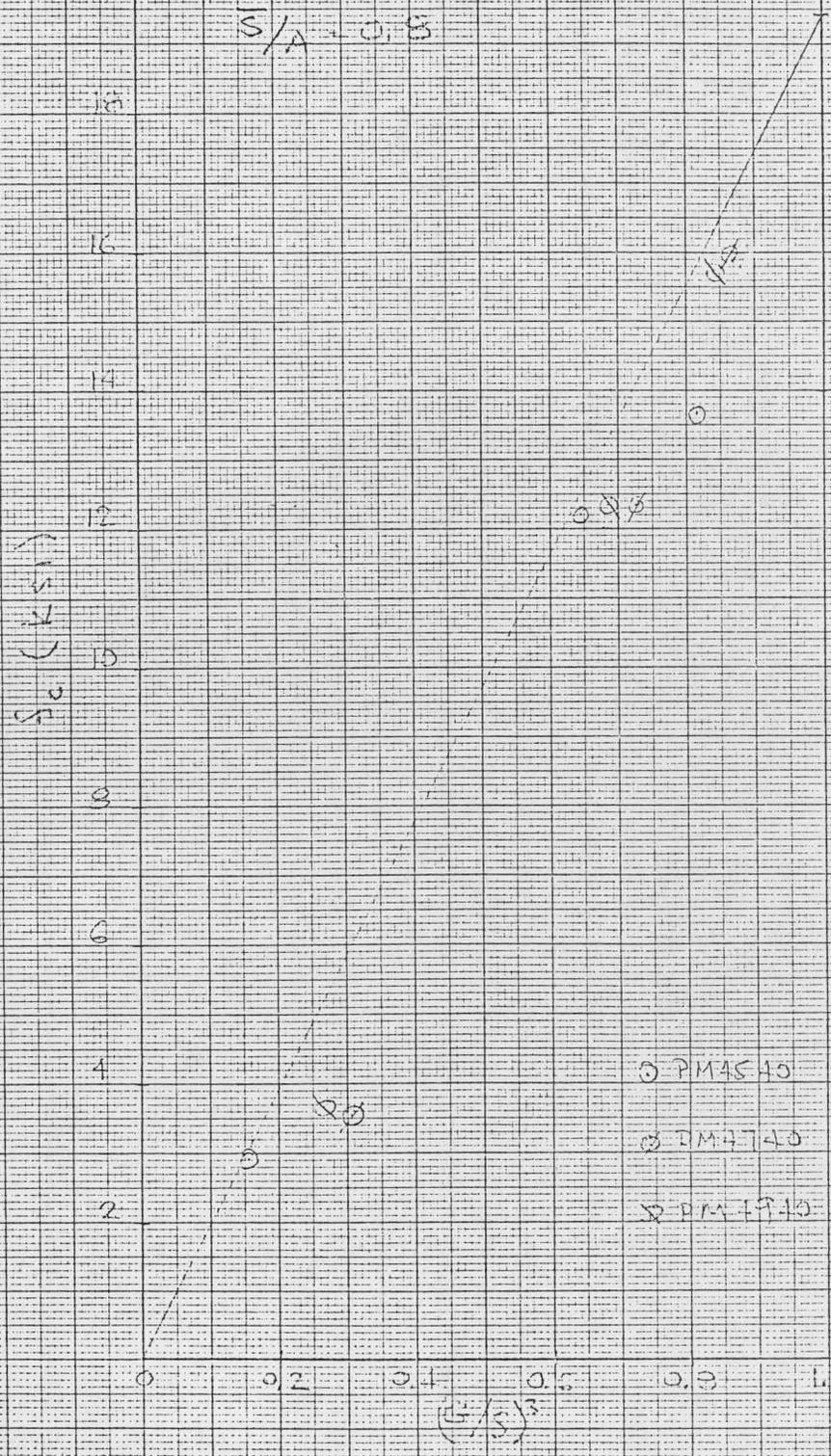


Fig. 16
48

MCC-275 + 7.6% GYPSUM
 < 30 MICRONS $w/c = 0.6$
 $S/A = 0.9$

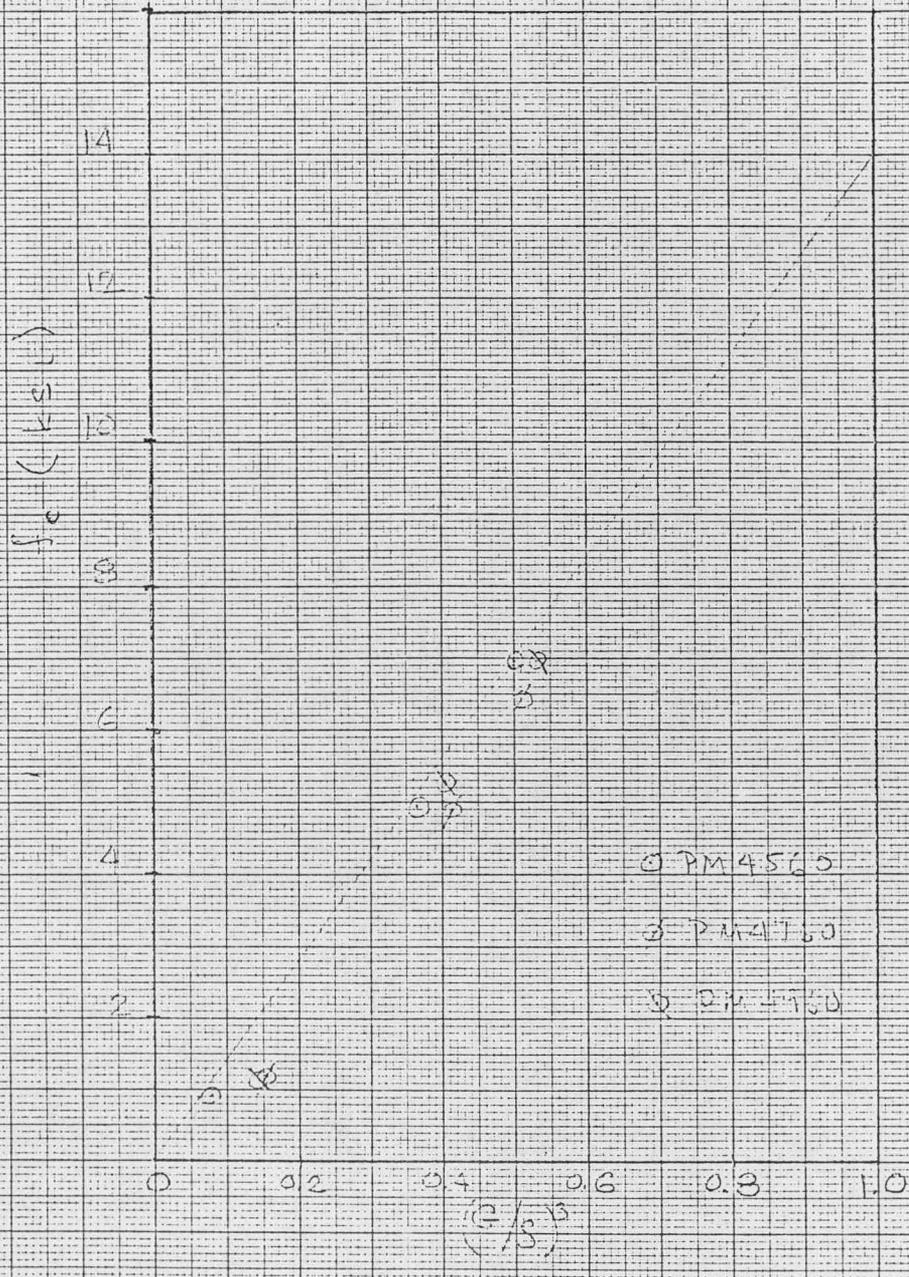


Fig. 17
 49

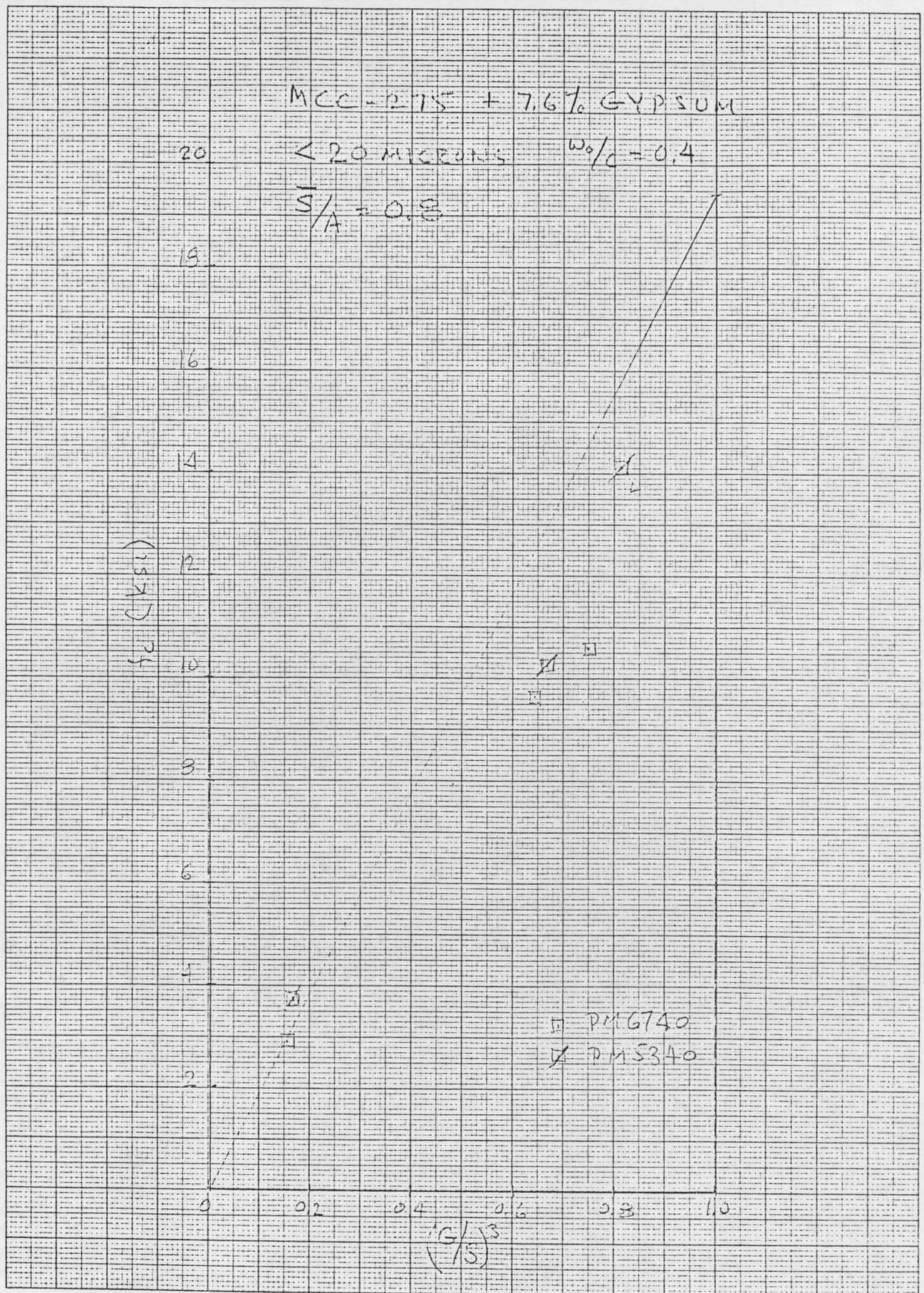


Fig. 18

MCC-2.75 + 7.6% GYPSUM

< 20 MICRONS $w_c/c = 0.6$

$\bar{S}/A = 0.8$

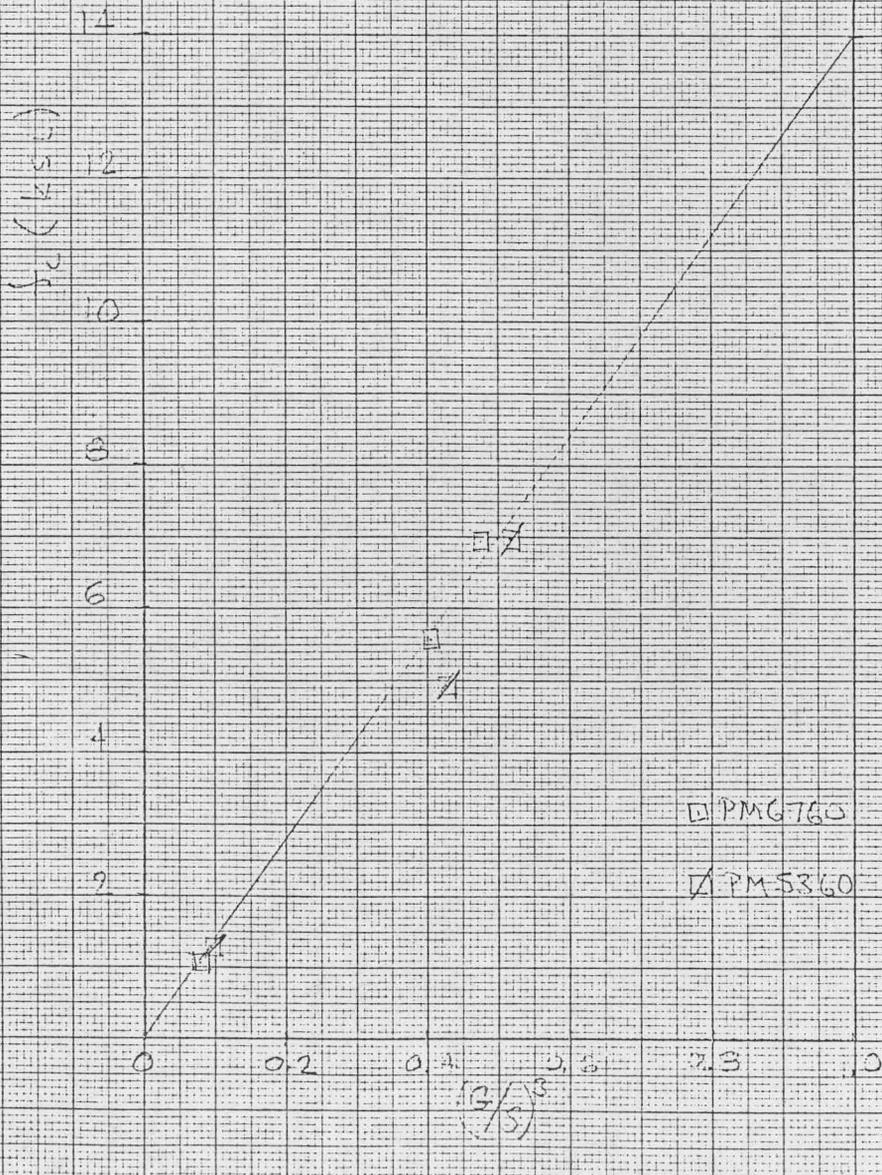


Fig. 19