GENERALIZED LOG-NORMAL DISTRIBUTION OF
PORE SIZES IN HYDRATED CEMENT PASTE

FEBRUARY 1971 - NUMBER 4

BY

SIDNEY DIAMOND
W. L. DOLCH

JHHRP

JOINT HIGHWAY RESEARCH PROJECT
PURDUE UNIVERSITY AND
INDIANA STATE HIGHWAY COMMISSION
Technical Paper

GENERALIZED LOG-NORMAL DISTRIBUTION OF PORE SIZES
IN HYDRATED CEMENT PASTE

TO: J. F. McLaughlin, Director
Joint Highway Research Project

FROM: H. L. Michael, Associate Director
Joint Highway Research Project

File No.: 5-14
February 2, 1971

Attached is a Technical Paper titled "Generalized Log-Normal Distribution of Pore Sizes in Hydrated Cement Paste." The paper has been authored by Professors Sidney Diamond and W. L. Dolch of our staff and has been offered to The Journal of Colloid and Interface Science for publication.

The paper reports research conducted by the authors as a special project of interest resulting from activities on regularly approved research projects. It is reported to the Board for information and for approval of publication.

Respectfully submitted,

Harold L. Michael
Associate Director

HLM:ms

cc: F. L. Ashbaucher
W. L. Dolch
W. H. Goetz
W. L. Grecco
M. J. Gutzwiller
G. K. Hallock

M. E. Harr
R. H. Harrell
M. L. Hayes
E. M. Mikhail
R. D. Miles
J. W. Miller

C. F. Scholer
M. B. Scott
W. T. Spencer
H. R. J. Walsh
K. B. Woods
E. J. Yoder
Technical Paper

GENERALIZED LOG-NORMAL DISTRIBUTION OF PORE SIZES IN HYDRATED CEMENT PASTE

by

Sidney Diamond

and

W. L. Dolch

Joint Highway Research Project

File No.: 5-14

Purdue University
Lafayette, Indiana
February 2, 1971
Generalized Log-Normal Distribution of Pore Sizes in Hydrated Cement Paste

by

Sidney Diamond and W. L. Dolch

School of Civil Engineering

Purdue University, Lafayette, Indiana 47907

ABSTRACT

Pore-size distributions of hardened cement pastes, as determined by mercury porosimetry, are shown to be generalized log-normal distributions bounded by the existence of a maximum diameter but not by a minimum diameter. An excellent fit is found for pastes of 0.4 and 0.6 water-cement ratio and ages between 1 day and almost 1 year. The distribution is described in terms of three parameters: the limiting upper bound diameter (M∞) and two parameters M* and δ, describing the geometric mean and standard deviation, respectively, of the generalized log normal distribution. The cumulative pore size distribution is given by the equation:

\[ P(M) = 50 - 50 \text{erf} \left( \frac{\ln \frac{M^*}{M}}{\sqrt{2} \ln \delta} \right) \]

where \( P(M) \) is percent of pore volume in diameters larger than \( M \), \( M^* \) is \( M \cdot M_\infty / M_\infty - M \), and \( \text{erf} \) is the error function. \( M_\infty \) and \( M^* \) are functions of the water/cement ratio; they decrease with age up to about 2 months and are then sensibly constant. Intrusion data taken at pressures...
50,000 psi, corresponding to diameters of the order of 25Å, substantiate the conclusion that all of the pores intruded belong to a single pore-size distribution; no evidence of bi-modality (i.e. the existence of a separate class of gel pores) is observed.
INTRODUCTION

The early work of Powers (1, 2) has long been interpreted as implying that hardened Portland cement paste (the reaction product of cement and water) has a bimodal pore-size distribution. It has been conventional to speak about "cement gel" as an entity constituting the products of the cement hydration, including the coarsely-crystalline lime. This gel is interpreted as having a characteristic or intrinsic porosity constituting about one-quarter of its bulk volume in so-called gel pores; these were calculated to be about 20 Å in diameter. In addition to cement gel, the hardened paste contains residual unreacted cement grains and also residual pore spaces (the so-called capillary pores) that were supposed to be of a size range "orders of magnitude larger than gel pores" (2). This distinction between gel pores and capillary pores and the assumed bimodal pore-size distribution it entails have been a salient feature of what has become known as the Powers model of cement paste.

Brunauer and his colleagues (for example 3-5) have made many noteworthy contributions to the experimental study of the pore systems in cement paste. Their data have been secured by adsorption and desorption measurements with nitrogen (and other vapors) and have been interpreted in several highly original and ingenious ways. The final results, presented as differential pore-size functions, showed clear maxima in the range of 35 Å or less. Of course, all these experiments are restricted to a maximum size range of the order of 300 Å. Sorption experiments
with vapors of larger molecules yielded essentially similar results (6),

Recently Winslow and Diamond (7) studied the distribution of pore sizes in cement paste by mercury porosimetry and concluded that most of the pore volume resides in pores between roughly 100 and 1000 \(\mu\) in diameter. These results were not dissimilar to those of others (8, 9) using the same method.

Previously published studies using mercury porosimetry have been limited to pores above about 85 \(\mu\) in diameter owing to limitations on the hydraulic pressure that could be exerted by the instruments available; thus the size range conventionally attributed to gel pores has not been accessible for study by this method.

The Powers model has recently been challenged by Feldman and Sereda (10, for example), who offered an alternate model. One of the chief features of this new model is the existence of interlayer water that is readily removable, and also readily replaceable after outgassing, in the calcium silicate hydrate that makes up most of the cement gel. This feature, if correct, calls for a reinterpretation of the original water vapor adsorption data on which the concept of gel pores was first developed.

None of the work so far reported with respect to pore size distributions has included an attempt to develop an analytical expression to fit the experimentally-observed pore-size distributions. This situation is in strong contrast to the analogous field of particle size distribution measurement; particle-size distributions have been fitted to mathematical expressions by many workers.
LOG-NORMAL DISTRIBUTIONS

It has long been known that the log-normal distribution function fits many experimentally-determined particle size analyses. Representative of early studies are papers by Hatch and Choate (11) and by Austin (12). To the knowledge of the writers, the extension to pore-size distribution data has not previously been made.

The log-normal distribution function can be described briefly in the following equations, with the development patterned after that of Irani (13) and Irani and Callis (14). Note that the function is of the form of a normal distribution, but the parameter that is normally-distributed is the logarithm of the diameter rather than the diameter itself.

The probability of occurrence of particles of a diameter \( M \) is given by

\[
f(M) = \frac{1}{\sqrt{2\pi} \ln \sigma} \exp \left[ -\frac{1}{2} \left( \frac{\ln M - \ln \bar{M}}{\ln \sigma} \right)^2 \right]
\]

(1)

where \( \bar{M} \) is the geometric mean diameter of the distribution and \( \sigma \) is the geometric standard deviation.

The geometric mean diameter \( \bar{M} \) is the diameter above which 50 percent of the particles lie:

\[
\int_{\bar{M}}^{\infty} f(M) \ d(\ln M) = \frac{1}{2}
\]

(2)

The geometric standard deviation is given implicitly by the expression:

\[
\int_{\bar{M}}^{\bar{M} \sigma} f(M) \ d(\ln M) = \int_{\bar{M}}^{\bar{M} \sigma} f(M) \ d(\ln M) = 0.3413
\]

(3)
The value of \( \sigma \) for a given distribution can be obtained from the experimental cumulative distribution data by dividing the diameter at 15.87 percent oversize by \( \bar{N} \), or alternatively, by dividing \( \bar{N} \) by the diameter at 84.13 percent oversize.

The utility of the function derives from a number of useful properties it possesses. First, in integrated form, it can be plotted as a straight line on log probability paper, i.e. paper ruled according to the normal probability function on one axis and a logarithmic scale on the other. The value of \( \bar{N} \) is read immediately from the value of the plot at the 50% probability line, and the value for \( \sigma \) is computed almost as easily by either of the methods mentioned above.

So far, the function has been framed in terms of a number distribution, which describes the probability of occurrence of individual particles of a given diameter. Another useful property of the log normal function is that number distributions are simply related to weight distributions: Kapteyn's law can be stated as:

\[
\ln \bar{N}_w = \ln \bar{N}_n + 3 \ln^2 (\sigma)
\]

(4)

where \( \bar{N}_w \) = the mean of the weight distribution
\( \bar{N}_n \) = the mean of the number distribution
\( \sigma \) = the geometric standard deviation of either distribution

(they are identical).

Kapteyn's law results in the happy circumstance that the two distributions plot as parallel straight lines, and graphical estimation of one from experimental determination of the other is straightforward.
MODIFIED LOG NORMAL DISTRIBUTIONS.

Occasionally particle-size distributions arise that do not fit the log-normal distribution. Some of these can be fitted satisfactorily to suitable modifications of a more general function that includes the log normal distribution as a special case.

One way in which distributions that require a modified treatment come about is if the process that generates the particles in question (for example, crystal growth from solution, or comminution by grinding) imposes either an upper or a lower bound to the size range. The log-normal distribution assumes no such bounding, i.e. that an increasingly small but finite probability is attached to sizes increasingly remote from the mean size, without limit. Practically speaking, if the mean of the distribution is distant from the limit, the linear relation between probability of occurrence and log of particle size is not much affected, but if the mean is close to one or the other of the limits, the form of the distribution of particles sizes must change, and the linear relation is modified.

Kottler (15) and Irani and Callis (14) have explored this situation analytically. The treatment below is patterned after that of the latter, with some modification.

The generalized log-normal distribution function is based on the postulate that what is log-normally distributed is not the particle diameter \( D \), but rather a function \( M^a \) of the particle diameter defined with respect to the upper and lower limits of the range as:
\[ \bar{M}^\ast = \frac{(M_\infty - M_0)}{(M_\infty - M)} \]  

where \( M_0 \) = the lower size limit of the distribution and \( M_\infty \) = the upper size limit of the distribution.

With this definition, the generalized log-normal distribution function is

\[ f(M) = \frac{1}{\sqrt{2\pi} \ln \sigma} \exp \left\{ -\left[ \frac{\ln \frac{M}{M_\infty}}{\sqrt{2} \ln \sigma} \right]^2 \right\} \]  

where the distribution parameters \( \bar{M}^\ast \) and \( \sigma \) now reflect the properties of the distribution of \( M^\ast \) rather than of the diameter \( M \).

The cumulative distribution function is obtained by integrating Equation 6:

\[ P(M) = 100 \int_{M}^{\infty} f(M) \ d\ln \left( \frac{M - M_0}{M_\infty - M} \right) \]  

The integral can be evaluated in terms of the error function to yield the following expression:

\[ P(M) = 50 - 50 \ \text{erf} \left[ \frac{\ln \frac{M}{M_\infty}}{\sqrt{2} \ln \sigma} \right] \]  

The form of Equation 8 is not identical to that given in references (6) and (7), in which an accidental error has appeared.

The results of examination of the distributions of the pore sizes of portland cement pastes suggests that a modified log-normal treatment of this type is required to fit the data. The lower limit of the experimental distribution (\( M_0 \)) is sufficiently distant from the mean to
have little consequence, but the upper limit \( M_\infty \) strongly influences the shape of the distribution curve, and its influence must be taken into account. In such cases, \( M_0 \) may be taken as zero, and the parameter \( M^* \) reduces to:

\[
M^* = \frac{M_\infty}{M_\infty - M}
\]  

(9)

METHOD OF FITTING OF PORE-SIZE DISTRIBUTION DATA

An example is now provided to illustrate the fitting of the generalized log-normal distribution function to pore-size distribution data of cement paste.

The cement paste was prepared at a water:cement ratio of 0.6 from a Type I Portland cement. It was mixed under vacuum, compacted in a reproducible manner, and hydrated for 2 days at 24°C under saturated lime-water. The density and total pore space were then determined, and the specimen was cured. Pore-size distribution determinations were made by mercury porosimetry, as previously described by Winslow and Diamond (7). A contact angle of 117° was used in calculating the results. Figure 1 presents the results of two separate determinations on replicate portions of this paste, one carried out in this laboratory using an Aminco-Winslow porosimeter of 15,000 psi pressuring capacity, the other carried out in the Applications Laboratory of the Micromeritics Instrument Corporation using a Micromeritics Instrument Corporation porosimeter of 50,000 psi pressuring capacity. The agreement of the two sets of data is excellent except in the range of sizes coarser than 1 \( \mu \text{m} \). The apparent content
of pores above this size is not generally reproducible and is at least partly due to artifact. For older pastes, or pastes of lower water/cement ratio, this non-reproducible coarse porosity becomes of even less quantitative importance, and for practical purposes it may be ignored.

The determination of the total pore space for this sample yielded a value of 0.430 cm$^3$/g, which is slightly in excess of the amount of mercury intruded at 50,000 psi pressure (0.402 cm$^3$/g). For more mature cement pastes the mercury intrusion is somewhat less complete.

The mercury pore size distribution data are normally expressed in terms of the cumulative volume of pore space intruded as a function of pore diameter. The cumulation is logically carried out from the largest diameters (intruded under the least pressure), downward to the smallest that can be intruded. The minimum size is set by the maximum pressuring capacity of the instrument. The volumes are usually expressed as volumes per gram of dry weight. The form of the distribution function to which it is desired to fit the data, Equation 8, is expressed in terms of percent probability of finding a volume unit as large or larger than a given size. In order to convert the experimental data to a suitable form, each cumulative intruded volume measurement is divided by the total volume of pore space present in the sample concerned. The data then express the cumulative distribution of volume in terms of diameter, normalized to 100 percent of the volume present (even though not all of it may be intruded). This is thus also the probability of finding a given volume unit in pores of size equal to or larger than that specified.
Figure 2 shows the data of Figure 1 normalized and plotted on log-probability paper. On such a plot a straight-line relation would indicate that the data fit the "simple" log-normal distribution. The data in fact do so, except that the straight-line relationship is lost for sizes above about 0.3 \( \mu m \). The trend of the data beyond this diameter curves to intersect the abscissa at a value slightly in excess of 0.8 \( \mu m \), if the points showing the non-reproducible porosity of the coarsest 3 percent or so of the distribution are ignored.

Such a plot defines "Case 4" as classified by Irani and Callis, i.e., the existence of a basically log-normal distribution perturbed at its upper end by some factor which limits the maximum size that can be present. In the present context, the factor is obvious; the maximum pore size is limited by the size of the interstices between the grains of unhydrated cement at the time of set.

The procedure for fitting the generalized log-normal function to the data consists of the following steps:

1) The intersection of the trend line with the diameter axis is taken as \( M_\infty \).

2) The parameter \( M^* \) is calculated for each experimental value of \( M \). In this case, as indicated by Equation 9, \( M^* \) is given by \( \frac{M \cdot M_\infty}{N_{\mu_1}} \). When normalized cumulative intrusion is plotted vs. \( \ln M^* \), the result should be a straight line.

3) If the initial estimate of \( M_\infty \) does not result in straight-line fit, several trials are made using slightly augmented or reduced estimates of \( M_\infty \) until a good fit is obtained.
Such a procedure applied to the data of the present illustration yields Figure 3, which is calculated for a $N_0$ of $0.82 \mu m$. The excellence of the fit is apparent, over 4 magnitudes of $N_0$. The next step is to determine the mean, $\bar{N}_0$ and the geometric standard deviation $\sigma$ of the log normal distribution of the "reduced" diameter $N_0$. From the intersection with the 50% probability line the mean is evaluated as 0.25 $\mu m$, and by the procedure previously outlined, the standard deviation is evaluated as 25. Note that this standard deviation is high, indicating a broad log-normal distribution, a fact which is qualitatively obvious from the spread of the "reduced" diameters.

We have now characterized the distribution of pore diameters in terms of a generalized or modified log normal distribution with an upper size limit of $0.82 \mu m$, the "reduced" diameter $N_0$ being distributed so as to have a mean of 0.25 $\mu m$ and a $\sigma$ of 25. Three questions then arise:

1) How good is the fit? 2) What do the parameters really mean? 3) Of what relevance are the results?

Table 1 gives the comparison of cumulative pore size distribution data calculated by inserting the fitted parameters into Equation 8, with the original experimental data. It is apparent that the equation fits both sets of experimental data with satisfactory precision.

The answer to the second question is slightly more complex. In essence, the log-normal distribution of $N_0$ is conceived as the log-normal distribution of $N$ that would have developed had there been no limitation on the maximum size of pore that could be present. In this sense the $N_0$
distribution is the "idealized" log-normal distribution. The individual values of \( N^* \) approach the corresponding values of \( M \) as one goes to small diameters far removed from the perturbing effect of the \( N^\infty \) limit. However, care must be taken in that physically one must be concerned with the actual, rather than the idealized, distribution. The actual distribution is not a simple log normal function. Its 50% probability diameter is not that characteristic of the \( N^* \) distribution, but something less than this. Similarly, the "spread" of the actual distribution is less than that implied by the \( \sigma \) value calculated for the idealized \( N^* \) distribution, being reduced or truncated on the upper side of the mean.

In answer to the third question, in its most restricted sense the equation can be treated simply as a means of expressing a given pore size distribution in analytcal form, so that computer or other mathematical manipulations can be carried out on it conveniently. This would be useful in itself, but undoubtedly many different mathematical expressions could be developed to fit a given set of experimental data. The real point of the present treatment is twofold: the parameters of the equation have physical significance, and the equation can be satisfactorily fitted to all mercury intrusion pore-size distributions of cement pastes so far examined.

RESULTS FOR OTHER PORTLAND CEMENT PASTES

The fit of the modified log-normal distribution function was examined for cement pastes of varying age and initial water:cement ratio. The pastes used were prepared in a manner similar to that described by Winslow.
and Diamond (7) but represented a different set, with pore size distributions similar, but not identical, to those previously reported. Most of the data represent determinations carried out in this laboratory in the range 0-15,000 psi. These are supplemented with a few runs in the 0-50,000 psi range carried out through the courtesy of the Micromeritics Instrument Corporation.

Figure 4 shows the fit observed for a series of 0.6 water:cement ratio pastes ranging in age from 1 day to 61 days. Changes are obviously rapid in the initial hydration period. However, after seven days the slope of the distribution function remains approximately constant, although the distribution continues to get finer and finer. Figure 5 shows superimposed data for 61 days, 182, and 318 days. After about 2 months the distribution function for these samples appears to be essentially constant.

Figure 6 shows similar data for a series of pastes hydrated at a water:cement ratio of 0.4. Figure 7 shows superimposed data for 61, 182, and 320 day old pastes, which again show what seems to be a common distribution, although the fit is not quite as good as that in Figure 5. The trend line is parallel to that of the 28-day old sample of Figure 6, suggesting that the change in slope between 14 days and 28 days in Figure 6 is real.

The parameters of the modified log-normal distribution equation estimated for each of the samples plotted in Figures 4 through 7 are given in Table 2, along with measured values of total pore space and maximum intrusion of mercury. The upper size limit \( M_\infty \) is, as expected,
Initially of the micrometer-size range (0.3 and 0.7 \( \mu m \), respectively, for the 0.6 and 0.4 water:cement ratio series). It decays in a few months to seemingly steady-state values of about 0.1 and 0.06 \( \mu m \), respectively. At all stages the 0.6 pastes have a higher upper limit than the 0.4 pastes.

The \( \overline{M}^k \) parameters also reduce with age, going from 0.6 and 0.17 \( \mu m \) respectively to about 0.015 and 0.006 \( \mu m \) after a few months. The geometric standard deviation apparently follows a different trend with time. The high initial values (50 and 24, respectively) decay to approximately their lower limits within a week: further aging does not materially reduce this parameter for the 0.6 pastes, and it increases the parameter for the 0.4 pastes to about 30.

The approximate constancy of the parameters for ages of 60 days and beyond is noteworthy. Since the pastes of this age are more than 90% hydrated, the data drawn from these and older pastes should be more or less consistent. One may thus consider that the mercury intrusion pore-size distributions of "mature" pastes can be described by Equation 8 using the characteristic parameters \( \overline{M}_\infty \approx 0.10 \mu m, \overline{M}_k \approx 0.015 \mu m, \sigma \approx 11 \) for 0.6 w:c pastes, and \( \overline{M}_\infty \approx 0.06 \mu m, \overline{M}_k \approx 0.006 \mu m, \) and \( \sigma \approx 30 \) for 0.4 w:c pastes.

There remains the problem that roughly one quarter of the pore space in mature 0.6 pastes is not intruded even at 50,000 psi pressure, corresponding to about 25 \( \AA \) in diameter. While comparable data are not available for the 0.4 paste series, extrapolation of the trend of Figure 7 suggests that the corresponding figure would be about 40%. As previously
mentioned, the pore space not filled by intrusion may be thought of as either in sizes too fine or with entryways too fine to be intruded, or else as larger pores which are "encapsulated" or otherwise unreachable by mercury. This point will be discussed later.
DISCUSSION AND IMPLICATIONS

With respect to subdivision of pore spaces, the processes of cement hydration may be regarded as somewhat analogous to the process of crushing or grinding with respect to particle size. The analogy is imperfect, for the total volume of pores diminishes as hydration proceeds, while the particle volume remains unchanged in particle comminution processes. Nevertheless, if one considers size distribution normalized to total pore volume at each stage, the hydration process can be considered to involve repeated subdivision of intergranular spaces into smaller and smaller units as hydration products repeatedly bridge the water-filled spaces. Such a process resembles the process of reduction of particle size by crushing and grinding.

The latter process has been known to result in log-normal particle size distributions for many years. Epstein (16), for example, showed mathematically that "under certain hypotheses the laws of probability operate in such a way that size distributions obtained from the continued repetition on the breakage process are asymptotically logarithmico-normal."

The fact that the pore size distributions under discussion are not simply log-normal but must be fitted to a generalized log-normal distribution function deserves comment. It should be recalled that all real particle or pore size distributions do, in fact, have some maximum size and some minimum size. In the present case, the maximum size,
\( (N_o) \) is always reasonably close to the geometric mean \( \bar{N}^s \). Initially, 
\( N_o \) is presumably set by the spaces left between grains of cement, 
already partly bridged over by hydration products at the time of set. 
This maximum size continues to decay with further hydration, as does 
the geometric mean diameter, but the former remains close enough to 
the latter at all stages of hydration so that the form of the distribu-
tion function is always affected.

A major implication of this study has to do with the problem of 
whether there is a separate class of "gel pores" in the range of tens 
of Angstroms as originally postulated by Powers (1) and generally 
accepted for many years. The present data contain three determinations 
that extend to the 25 Å diameter range, if the assumptions of the 
mercury intrusion method are correct. None plot above the log-normal trend. 
The log-normal plot for two of these, the 2-day old and the 28 day-old 
are shown as dark squares in Figure 4. For the mature paste (318 days 
old), the pore volume intruded below about 60 Å in diameter is not only 
less than that predicted by the log-normal plot, but is almost negligible 
in absolute terms. The plot of cumulative percentage of pore volume 
intruded vs. pore diameter is given in Figure 8 for this sample. The 
total pore volume in this sample was measured as 0.306 cm\(^3\)/g. The volume 
intruded between pressures corresponding to pore diameters of 77 Å and 
8 Å is only 0.011 cm\(^3\)/g.
Admittedly, at the maximum pressure exerted about 25 percent of the pore space was not intruded. The reason for this has not yet been demonstrated with certainty. Some of the untallied pores may have entryways too narrow to penetrate with mercury at 50,000 psi, and some of them may be in calcium silicate hydrate regions that are isolated from the outside as a result of encapsulation by secondary deposits of calcium hydroxide growing through the mass. Visual evidence that this encapsulation happens has been published earlier (17) in the form of scanning electron micrographs.

Despite this uncertainty, the present results are clear. On the basis of the experimental evidence, all of the pore volume intruded constitutes a single modified log-normal distribution of diameters, and no evidence for the existence of a separate class of characteristic "gel" pores is found.
ACKNOWLEDGEMENTS

The work reported here was carried out with support by the Indiana State Highway Commission through the Joint Highway Research Board, Purdue University. We thank our colleague, W. H. Perloff, for the correct mathematical derivation of Equation 8. The courtesy of the Micromeritics Instrument Corporation in running the 0-50,000 psi determinations is acknowledged with thanks.
REFERENCES


<table>
<thead>
<tr>
<th>M (pore diam.), Åm</th>
<th>Calculated</th>
<th>Experimental 0-15,000 psi run</th>
<th>Experimental 0-50,000 psi run</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.703</td>
<td>17.8</td>
<td>17.1</td>
<td>-</td>
</tr>
<tr>
<td>0.615</td>
<td>24.9</td>
<td>25.1</td>
<td>-</td>
</tr>
<tr>
<td>0.512</td>
<td>29.9</td>
<td>-</td>
<td>29.4</td>
</tr>
<tr>
<td>0.492</td>
<td>31.1</td>
<td>33.9</td>
<td>-</td>
</tr>
<tr>
<td>0.410</td>
<td>35.6</td>
<td>38.4</td>
<td>33.8</td>
</tr>
<tr>
<td>0.324</td>
<td>40.7</td>
<td>43.8</td>
<td>38.6</td>
</tr>
<tr>
<td>0.300</td>
<td>42.2</td>
<td>-</td>
<td>46.1</td>
</tr>
<tr>
<td>0.241</td>
<td>46.4</td>
<td>50.8</td>
<td>52.8</td>
</tr>
<tr>
<td>0.224</td>
<td>47.5</td>
<td>53.8</td>
<td>58.4</td>
</tr>
<tr>
<td>0.176</td>
<td>51.4</td>
<td>60.4</td>
<td>60.0</td>
</tr>
<tr>
<td>0.146</td>
<td>54.3</td>
<td>-</td>
<td>62.3</td>
</tr>
<tr>
<td>0.137</td>
<td>55.2</td>
<td>66.6</td>
<td>67.3</td>
</tr>
<tr>
<td>0.103</td>
<td>59.3</td>
<td>67.8</td>
<td>68.9</td>
</tr>
<tr>
<td>0.095</td>
<td>60.4</td>
<td>70.5</td>
<td>72.5</td>
</tr>
<tr>
<td>0.0820</td>
<td>62.3</td>
<td>73.8</td>
<td>75.4</td>
</tr>
<tr>
<td>0.0630</td>
<td>66.6</td>
<td>79.3</td>
<td>78.0</td>
</tr>
<tr>
<td>0.0615</td>
<td>67.8</td>
<td>80.5</td>
<td>78.0</td>
</tr>
<tr>
<td>0.0439</td>
<td>70.5</td>
<td>82.4</td>
<td>82.1</td>
</tr>
<tr>
<td>0.0410</td>
<td>70.8</td>
<td>83.1</td>
<td>-</td>
</tr>
<tr>
<td>0.0307</td>
<td>73.8</td>
<td>83.8</td>
<td>-</td>
</tr>
<tr>
<td>0.0166</td>
<td>79.3</td>
<td>83.8</td>
<td>-</td>
</tr>
<tr>
<td>0.0154</td>
<td>80.5</td>
<td>83.8</td>
<td>-</td>
</tr>
<tr>
<td>0.0123</td>
<td>82.4</td>
<td>84.2</td>
<td>-</td>
</tr>
<tr>
<td>0.0112</td>
<td>83.1</td>
<td>-</td>
<td>85.8</td>
</tr>
<tr>
<td>0.0102</td>
<td>83.8</td>
<td>-</td>
<td>87.6</td>
</tr>
<tr>
<td>0.0087</td>
<td>85.1</td>
<td>-</td>
<td>90.9</td>
</tr>
<tr>
<td>0.0077</td>
<td>86.0</td>
<td>-</td>
<td>90.9</td>
</tr>
<tr>
<td>0.0056</td>
<td>88.0</td>
<td>-</td>
<td>91.5</td>
</tr>
<tr>
<td>0.0041</td>
<td>89.9</td>
<td>-</td>
<td>93.5</td>
</tr>
<tr>
<td>0.0032</td>
<td>91.1</td>
<td>-</td>
<td>93.5</td>
</tr>
<tr>
<td>0.0025</td>
<td>92.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Calculated from Equation 8, using $M_0 = 0.82$, $M_1 = 0.25$, $d = 25$
Table 2

GENERALIZED LOG-NORMAL DISTRIBUTION
PARAMETERS OF CEMENT PASTES AS A FUNCTION OF AGE AND WATER-CEMENT RATIO

<table>
<thead>
<tr>
<th>W/C RATIO</th>
<th>AGE (Days)</th>
<th>TOTAL POROUS SPACE (cm³/g)</th>
<th>MAXIMUM VOLUME INTRUDED (cm³/g) 15,000psi</th>
<th>50,000psi</th>
<th>FITTED PARAMETERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>1</td>
<td>0.469</td>
<td>0.404</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.430</td>
<td>0.362</td>
<td>0.401</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.392</td>
<td>0.303</td>
<td>-</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>0.350</td>
<td>0.226</td>
<td>0.269</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>61</td>
<td>0.309</td>
<td>0.182</td>
<td>-</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>182</td>
<td>0.314</td>
<td>0.183</td>
<td>-</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>0.306</td>
<td>0.188</td>
<td>0.225</td>
<td>0.12</td>
</tr>
<tr>
<td>0.4</td>
<td>1</td>
<td>0.313</td>
<td>0.254</td>
<td>-</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.310</td>
<td>0.239</td>
<td>-</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.259</td>
<td>0.175</td>
<td>-</td>
<td>0.085</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>0.244</td>
<td>0.140</td>
<td>-</td>
<td>0.085</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>0.200</td>
<td>0.104</td>
<td>-</td>
<td>0.064</td>
</tr>
<tr>
<td></td>
<td>61</td>
<td>0.188</td>
<td>0.083</td>
<td>-</td>
<td>0.055</td>
</tr>
<tr>
<td></td>
<td>182</td>
<td>0.187</td>
<td>0.083</td>
<td>-</td>
<td>0.057</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>0.187</td>
<td>0.087</td>
<td>-</td>
<td>0.064</td>
</tr>
</tbody>
</table>
Figure 1. Cumulative pore-size distributions for cement paste, 0.6 w/c ratio,
2 days old.
Figure 2. Log-normal Probability Plot for Data of Figure 1.
Figure 3. Generalized log-normal Probability Plot for Data of Figure 1, Assuming $N_{wc} = 0.02 \mu m$. 

0.6 W/C RATIO PASTE
2 DAYS

○ 0-15000 PSI RUN
■ 0-50000 PSI RUN
Figure 5. Generalized Log-Normal Probability Plot for Mature Cement Pastes of 0.6 w/c Ratio.
Figure 6. Generalized Log-normal Probability Plot for Cement Pastes of 0.4 w/c Ratio and Ages Between 1 Day and 28 Days.
Figure 6. Cumulative Mercury Pore Size Distribution for 0.6 w/c Paste 31 Days Old.