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SUB-DISTRIBUTIONS OF PORE SIZE: A NEW APPROACH TO CORRELATE PORE STRUCTURE WITH PERMEABILITY

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ABSTRACT

A typical cement paste pore-size distribution from mercury intrusion porosimetry has a hysteresis loop during an intrusion - extrusion - reintrusion cycle. The hysteresis can be eliminated merely by selecting an appropriately smaller receding contact angle. This allows one to subdivide the total pore-size distribution into two sub-distributions: one reversible and one irreversible. These sub-distributions were found for a series of cement pastes having w/c between 0.32 and 0.60 and ages between 1 and 30 days. In addition, the chloride permeabilities of the pastes were determined. This permeability was found to correlate more closely with the reversible sub-distribution than with either the total or the irreversible distributions. Specifically, it was found that the threshold diameter and intrusion volume of the reversible sub-distribution were the parameters that were best related to the permeability. This is presumably because the threshold pore diameter of the reversible sub-distribution represents the largest continuous path through the most accessible part of the pore system.

INTRODUCTION

The properties of portland cement paste are mostly dominated by its pore structure. This pore structure can be measured by several techniques, but mercury intrusion porosimetry has been the predominant one. During the mercury intrusion process, mercury is forced into a specimen from the surface toward the center. In practice, almost no pore systems have a uniform size or a size that gradually diminishes from the surface toward the center. There are generally constrictions that limit entry to the interior pore volume. Thus, the typical pore-size distribution obtained by intrusion is a distribution of true pore volume vs. pore entry sizes.

It is likely that fluid flow and permeability are also controlled by pore entry sizes. Therefore, the distribution from mercury intrusion may more closely define the operant pore system for permeability than the 'true' distribution of pore volume with 'true' pore size. Thus, one would expect that some aspect or aspects of an intrusion-based pore size distribution would correlate well with a paste's permeability.

Many newer porosimeters can monitor both mercury intrusion and extrusion from samples. When this is done, a hysteresis loop in the pore-size distribution is observed. It has been suggested [1,2] that this loop can be used to divide the total distribution into two sub-distributions that represent the parts of the pore system that can be reversibly and irreversibly intruded. One of these sub-distributions may better correlate with important properties of the paste than does the total pore-size distribution. It is the purpose of this paper to test this proposal with regard to the chloride permeability of a variety of cement pastes.

HYSTERESIS IN PORE-SIZE DISTRIBUTIONS FROM MERCURY INTRUSION

The phenomenon of hysteresis in pore-size distributions has been reported frequently. Several possible explanations have been proposed [3,4,5]. A typical example of hysteresis is shown in Fig. 1. It can been seen that part of the mercury is permanently trapped in the sample by the initial (first) intrusion. Whatever the reasons for this trapping of mercury, Lowell and Shields [5] found that the reason for the hysteresis between the extrusion and the second intrusion is merely the difference between the advancing and receding contact angles for mercury. And, they found that the hysteresis could be completely eliminated by selecting a properly smaller angle for the extrusion.

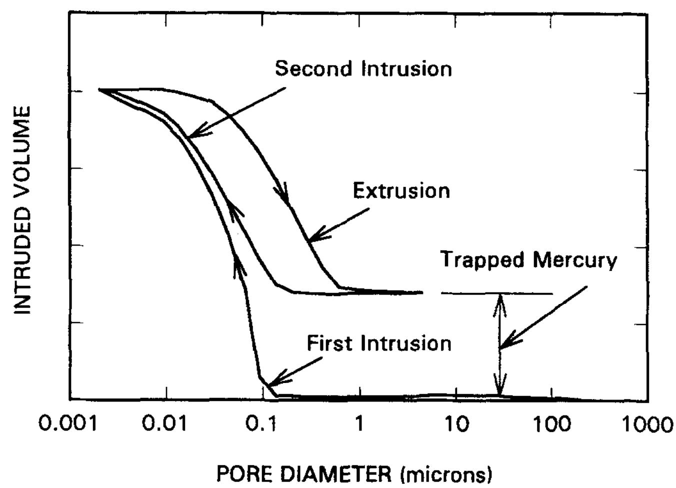


Fig. 1 Hysteresis Loop in Pore-Size Distribution Obtained from Mercury Porosimetry

If the hysteresis can be eliminated in this way, it means that the extrusion curve and the subsequent intrusion curves represent the same pore-size distribution. These curves will coincide if they are plotted with the appropriate contact angles. It has been suggested [1,2] that the second intrusion represented that portion of the total pore-size distribution that can be reversibly intruded. When this reversible distribution is subtracted from the total intrusion, the result is a second, sub-distribution that represents that part of the pore system that is irreversibly filled.

EXPERIMENTAL WORK

This study was planned to measure the pore structure and the chloride permeability of cement pastes with two variables: hydration age and water/cement ratio. At predetermined ages, the pore structures of the paste samples were determined by mercury intrusion porosimetry. And, the chloride permeabilities of the samples were measured according to AASHTO T277-83 [6].

Materials and Sample Preparation

ASTM Type I portland cement was used to prepare pastes at four water/cement ratios: 0.32, 0.40, 0.50, and 0.60. The w/c of 0.32 was the minimum at which the cement paste could be mixed properly in a vacuum mixer and cast easily without extra measures such as adding superplasticizers. All mixing was done in an evacuated chamber (vacuum mixer) to minimize the amount of entrapped air so that the pore space in the pastes could be considered as coming from the hydration process only. The mixing was done on a paint shaker. The paste samples were cast in cylindrical plastic molds (25 mm diameter × 280 mm long) for pore structure testing, and in steel molds (95 mm diameter × 300 mm long) for chloride permeability testing. After storage in a fog room for one day, the samples were demolded and put into lime-saturated water at room temperature until the test date. The range of hydration ages was from 1 to 30 days.

At the predetermined ages, the pore structure samples were taken out of the lime water, and broken into smaller pieces for intrusion. They were then dried in an oven at 105 °C for at least 24 hours. The permeability samples were cut with a diamond saw into 51 mm thick slices for chloride permeability testing. They were then coated around the perimeter with a two-part, rapid setting sealant.

Pore Structure Determination

The pore structures of the samples were obtained by mercury intrusion porosimetry using a pressuring cycle that caused intrusion, extrusion and finally re-intrusion. The minimum intruding pressure was 0.5 psia, and the maximum was 60,000 psia for the initial intrusion step. Because of instrumental limitations, the extrusion and the re-intrusion steps had applied pressures only between 29 to 60,000 psia. This discrepancy in pressure ranges had little effect on the data because the samples had virtually no intrusion at pressures less than 29 psia. The assumed advancing contact angle was 116° [7], and the assumed surface tension for mercury was 480 dynes/cm. Thus, the corresponding range of pore diameters was between about 244 μm and 20 Å for the initial intrusion, and between about 4.2 μm and 20 Å for the extrusion and second intrusion.

Calculation of Total, Reversible and Irreversible Distributions

The initial intrusion curve gave the total intrudable pore-size distribution. It was found that the extrusion and second intrusion curves could be superimposed by selecting an appropriately smaller receding contact angle for extrusion. This implies that the second intrusion is the reversible portion of the total intrusion distribution. It might be called the "reversible pore-size distribution". It is merely the distribution obtained during the second pressurization or intrusion. The rest of total distribution is associated with the portion of mercury that is irreversibly intruded. This might be called the "irreversible pore-size distribution". It can be obtained by subtracting the second intrusion curve (the reversible distribution) from the initial intrusion curve (the total distribution). All distributions in this study were calculated with software developed for this purpose by the authors.

Calculation of Threshold Diameters

One characteristic of the pore size distribution of cement paste is the "threshold diameter". In qualitative terms, this is the largest pore diameter at which significant intruded pore volume is detected. Its determination always requires some judgment as to exactly what level of intrusion is considered to be "significant". Sometimes the threshold diameter appeared to lie on an experimental data point, and its numerical value could be determined easily. However, in most cases the point appeared to fall between two experimental data points. In these cases, tangents were drawn on the cumulative distribution curve at the smallest diameter that did not exhibit significant intrusion and the largest diameter that did. The diameter corresponding to the intersection of these lines was taken as the threshold diameter.

Chloride Permeability Test

The chloride permeability was determined in accordance with AASHTO Test T277-83 [6]. Only Step 6 (conditioning) in the method was omitted because the samples in this study were stored in lime-saturated water until testing and conditioning was unnecessary. The test involves measuring the amount of electrical current that passes through a 95 mm diameter by 51 mm thick disk of material when one end of the disk is immersed in a sodium chloride solution and a potential difference of 60 V dc is maintained across the specimen for 6 hours. The total charge passed, in coulombs, is related to chloride permeability.

RESULTS AND DISCUSSION

Chloride Permeability

The relationship between the measured chloride permeability and age of hydrated cement paste with various w/c is shown in Fig. 2. For w/c greater than 0.32 the chloride permeability decreases with increasing age. For w/c = 0.32, the chloride permeability is almost constant for the different ages that were tested.

The w/c of 0.32 was the minimum at which the cement paste could be mixed and cast easily without using a superplasticizer. One was not used so that the only variables among pastes would be w/c and age.

The essentially constant chloride permeability of the w/c = 0.32 pastes might be considered a baseline value for this sample suite of pure cement pastes. It seems that this permeability is a characteristic of the material. The additional permeability of pastes with greater w/c appears to be associated only with the additional water used in the mixing. Thus, it seemed appropriate to analyze the results in terms of just this added permeability. It was calculated as the difference between the suite-characteristic value for w/c = 0.32 and the value for any other w/c.

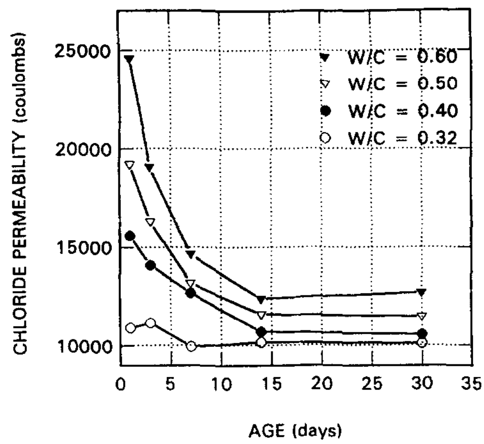
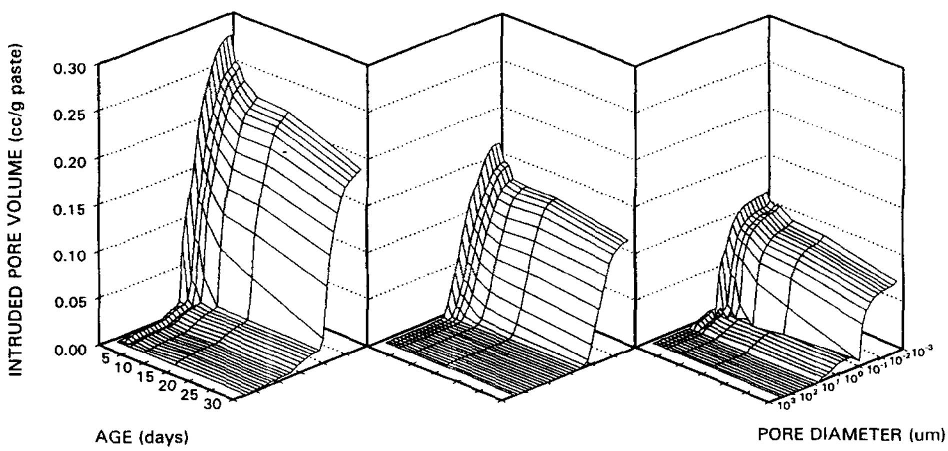


Fig. 2 Chloride Permeability of Hydrated Cement Pastes with Various W/C Ratios

Pore Structure Characterization

The total, reversible, and irreversible pore-size distributions were found for each paste by the approach described earlier. Figs. 3(a), (b) and (c) show the typical pattern of these distributions for the 0.50 w/c pastes. The distributions of other w/c pastes have similar patterns.



(a) Total (b) Reversible (c) Irreversible

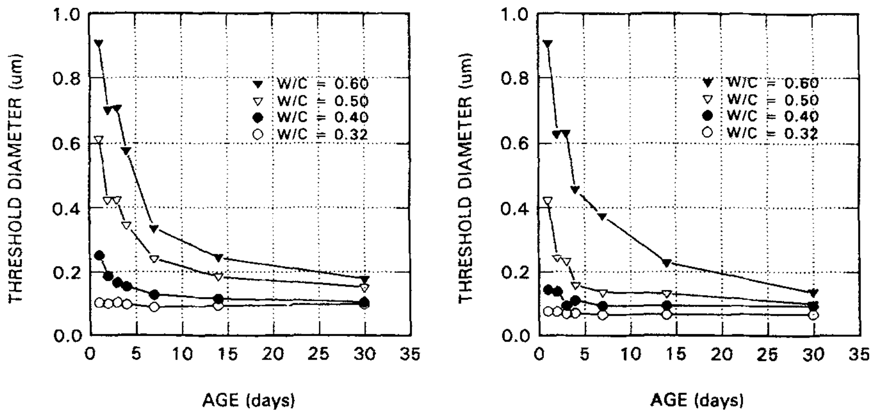
Fig. 3 Total, Reversible and Irreversible Pore-Size Distributions of Hydrated Cement Pastes with the 0.5 W/C Ratio

The thrust of the work reported here was to identify some aspect or parameter of the pore size distribution that correlated well with the chloride permeability. And, to see if a better correlation could be obtained if the aspect in question came from one of the two sub-distributions rather than the total distribution.

A number of parameters associated with the distributions were considered. Among these were: median pore diameter, total intruded volume, etc. In the end, two distribution parameters stood out as having the best correlation with the chloride permeability. These were: the threshold diameter and the cumulative intruded pore volume at the threshold diameter. Because of this, only these two will be discussed further.

Threshold Diameter vs. Chloride Permeability Relationship

The threshold diameters of all the distributions were calculated as described above. Fig. 4(a) shows the threshold diameters of the reversible distributions and Fig. 4(b) has those of the total distributions. Both of these figures show that the trends in changing threshold diameter with w/c and age are similar to the trends for the chloride permeability. The threshold diameters of the irreversible distributions did not show such a trend and will not be considered here.



(a) Reversible Distribution (b) Total Distribution

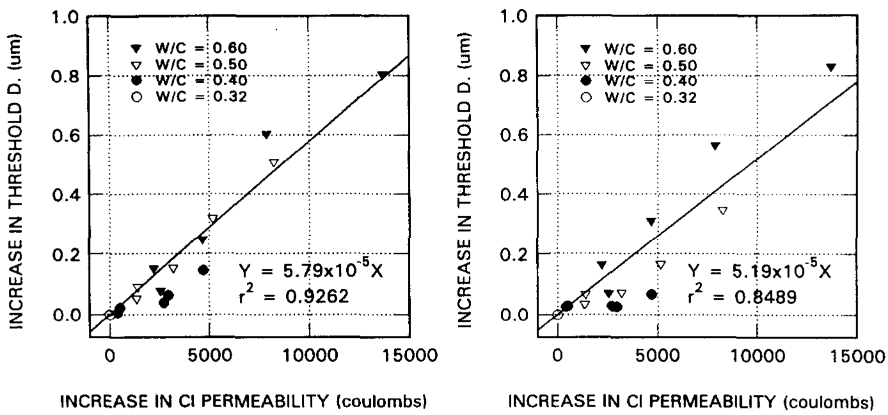
Fig. 4 Threshold Diameter vs. Age Relations

In a manner analogous to the treatment of the chloride permeability data, the threshold diameters for the 0.32 w/c paste can be taken as a reference, or baseline. And, one can find the increase in threshold diameter due to the added mix water in greater w/c pastes. This increase in threshold diameter is plotted against the increase in chloride permeability in Figs. 5. Fig 5(a) shows the data from the reversible distributions and Fig 5(b) the data from the total distributions. Both plots suggest a linear relationship of the form:

$$y = ax \qquad (1)$$

where y = increase in threshold diameter (μm), x = increase in chloride permeability (coulombs), and a is an empirical constant. In the case of Fig. 5(a), linear regression gives a value for a of 5.79×10^{-5}. The corresponding R squared value is 0.9262. Fig. 5(b) shows a poorer correspondence between increase in chloride permeability and increase in total threshold diameter. The R squared value is only 0.8489.

These results suggest that chloride permeability is most closely associated with just the reversible threshold diameter. For hydrated cement paste with 0.32 w/c, the chloride permeability is independent of age, and is associated with the essentially constant threshold diameter at all ages. Further, the increase in chloride permeability for larger w/c is associated with an increase in the reversible threshold diameter. The results suggest that chloride permeability is less directly associated with the threshold diameter of the total intrusion distribution. Thus, better predictions and modeling of chloride permeability can be expected if one uses the reversible sub-distribution.



(a) Reversible Distribution (b) Total Distribution

Fig. 5 Relationships between Increases in Chloride Permeability and Threshold Diameter

Pore Volume vs. Chloride Permeability Relationship

It has been observed that the reversible and total threshold diameters for w/c 0.32 pastes are essentially independent of age. These are the approximate minimums that the pastes can have without superplasticizers. The approximate values for these minimum threshold diameters are 0.135 µm for the reversible sub-distribution and 0.0633 µm for the total intrusion distribution.

At these diameters, the w/c 0.32 paste distributions have a very small intrudable pore volume. But, at these same diameters, pastes with greater w/c do have significant intrudable pore volumes. This situation is schematically displayed in Fig. 6. Pastes with w/c > 0.32 have an intrudable pore volume at the characteristic threshold diameter of the w/c = 0.32 paste. This might be called the "increased threshold pore volume".

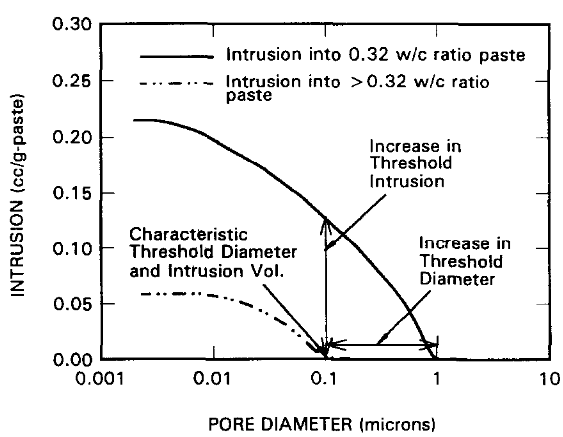
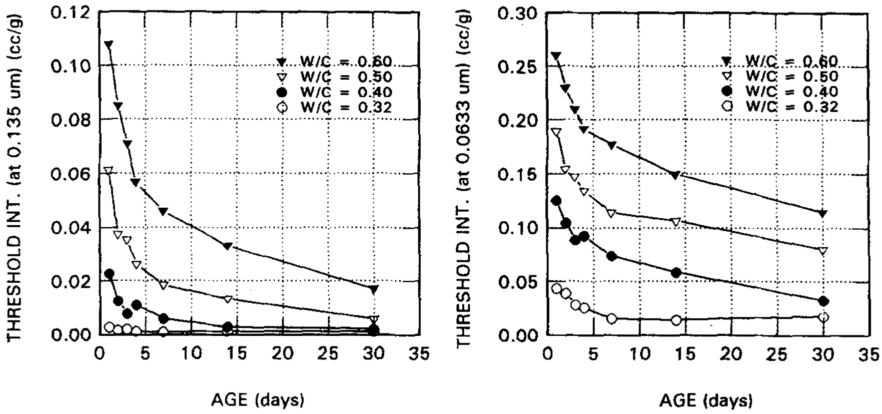


Fig. 6 Schematic Diagram Showing Ideas of Threshold Diameter and Threshold Intrusion Volume

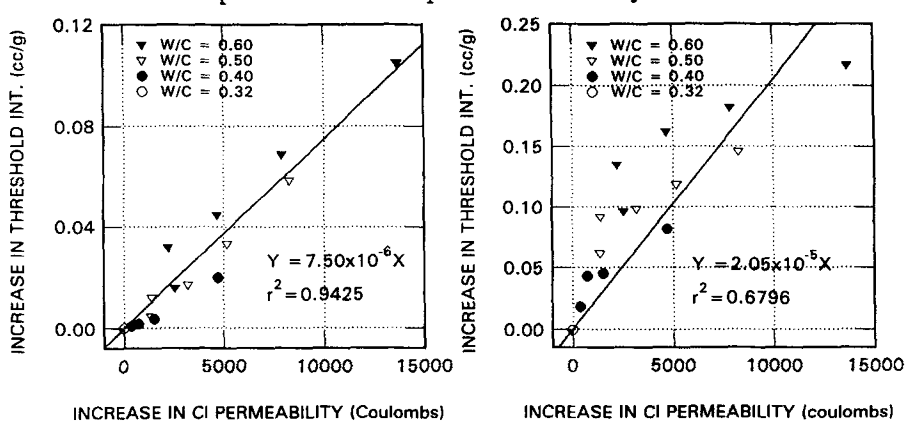
Fig. 7(a) gives the paste age vs. increased threshold pore volume of the reversible distributions. It shows that, for w/c = 0.32, the threshold intrusion is essentially constant and can be considered as a characteristic of the paste. For larger w/c, the extra intrusion at the 0.32 paste threshold displays a similar trend to that of age vs. the chloride permeability in Fig. 2. Fig. 7(b) shows the pattern for the increased intrusion of the total distributions. But the similarity in appearance to the plots in Fig. 2 is poorer.



(a) Reversible Distribution (b) Total Distribution

Fig. 7 Threshold Intrusion vs. Age Relations

As was done with the threshold diameters, the correlation between the increase in chloride permeability and the increase in threshold intrusion of the reversible distributions is shown in Fig. 8(a). The relation can be simply expressed by a linear equation similar to Eqn. 1. In the case of Fig. 8(a), the value of a is $7.50x10^{-6}$ and the R squared value is 0.9425. A similar plot using the increased threshold intrusion from the total distributions is shown in Fig. 8(b). Here the correlation is much poorer with an R squared value of only 0.6796.



(a) Reversible Distribution (b) Total Distribution

Fig. 8 Relationships between Increases in Chloride Permeability and Threshold Intrusion Volume

These results suggest that chloride permeability is most closely associated with just the increased threshold intrusion of the reversible distributions. For hydrated cement paste with 0.32 w/c, chloride permeability is independent of age, and is associated with the essentially constant threshold intrusion at all ages. Further, the increase in chloride permeability for larger w/c is associated with an increase in the threshold intrusion of the reversible distributions. They suggest that chloride permeability is much less well associated with the increased threshold intrusion of the total distributions.

Threshold Diameter vs. Pore Volume Relationship

The ideas of threshold diameter, threshold intrusion pore volume and increases in these quantities were illustrated schematically in Fig. 6. The distribution for a paste with w/c > 0.32 is shifted to the right on the diameter axis. This increases both its threshold diameter and its threshold intrusion volume relative to the w/c = 0.32 paste.

The good correspondence of chloride permeability with both of these parameters for the reversible sub-distributions infers that they are related. This relationship is shown in Fig. 9. It appears that, for the range of pastes in the study, the threshold diameter and threshold intrusion volume increase in proportion to each other. Thus, increasing the reversible threshold diameter by adding more mix water also proportionately increases the reversible threshold intrusion and either has the same effect on chloride permeability.

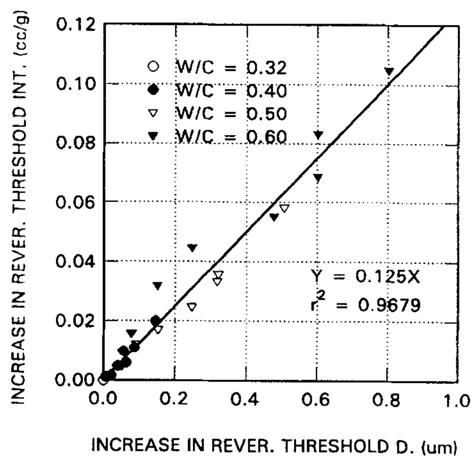


Fig. 9 Relationship between Increases in Threshold Diameter and in Threshold Intrusion Volume

SUMMARY AND CONCLUSIONS

The apparent hysteresis loop between mercury extrusion and subsequent re-intrusion for cement paste has been found to be due solely to differences in the advancing and receding contact angles. This allows one to subdivide the total intrusion pore size distribution into two sub-distributions. One of these corresponds to the reversible intrusion and might be expected to be associated with the more accessible part of the pore system. The other sub-distribution is associated with the irreversible intrusion and most likely represents the less accessible part of the pore system.

The threshold diameter is an aspect of most cement paste pore size distributions. It is approximately the largest pore diameter that is continuous throughout solid. The threshold diameter of the reversible sub-distribution is likely to represent the largest continuous channel size of the most accessible part of the pore system.

This threshold diameter and the corresponding intrusion of the reversible sub-distribution appear to have a constant, characteristic value that is independent of age for pastes of low (0.32) water to cement ratio. The constant chloride permeability of such pastes is associated with this characteristic pore diameter and volume.

Pastes with higher water to cement ratios have reversible sub-distributions with increased threshold diameters and increased threshold intrusions. The increased chloride permeability of these pastes is most closely correlated with these pore diameters and volumes. This is probably because the reversible threshold pore size is the widest, most accessible, path for fluid transport in the paste.

It is the reversible sub-distribution, and not the total nor the irreversible, that provides the best correlation with chloride permeability. Thus, the concept of subdividing a pore size distribution seems to have utility. This same concept may be equally advantageous when considering other aspects of cement paste.

ACKNOWLEDGMENTS

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