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A Review of the Pore Structure of Cement Paste and Concrete and its Influence on Permeability

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Synopsis: The permeability of hardened cement paste is reviewed with particular reference to the influence of pore structure. Permeability is usually modelled by applying D'Arcy's Law, although permeability measurements and pore size distributions determinations reveals the strong influence of large capillary pores (macropores) on flow through cement paste. The macropores form a continuous flow path within the paste. The effects of curing temperature, drying and admixtures on permeability can be understood in terms of their influence on macropores. Paste containing fly ash show anomalous behavior which apparently arises from internal damage occurring during pore structure It appears that the presence of fly ash promotes measurements. the formation of a discontinuous macropore system which inhibits flow.

<u>Keywords</u>: admixtures; calcium chlorides; <u>cement pastes;</u> <u>concretes</u>; fly ash; <u>hardened paste structure</u>; <u>permeability</u>; <u>porosity</u>; slags; water-reducing agents

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INTRODUCTION

Permeability is an important property with regard to the durability of concrete. It represents the ease with which water (or other fluids) can move through concrete, thereby transporting aggressive agents. It is thus of critical importance for many types of distress experienced by concrete. For example:

sulfate attack	-	movement of sulfate ions into
		concrete where adverse chemical
		reactions occur.
frost resistance	-	flow of water to relieve stresses
		caused by ice formation.
alkali-aggregate attack	-	movement of alkali ions to aggre-
		gates and water to swelling gels.
fire resistance	-	escape of steam from heated
		layers causing spalling.
corrosion of steel	-	movement of chloride ions to the
		surface of the steel.

PORE STRUCTURE

Since fluid flow takes place in the pore system it is first necessary to examine the pore structure in concrete. Pores in normal-weight concrete are considered part of the paste fraction and cover a very large size range (Figure 1). The traditional classification, suggested by Powers and Brownyard [1], considers two classes of pores: gel pores are associated with the formation of the hydration products ("cement gel"), which is the intrinsic porosity, while capillary pores are considered to be the remnants of water-filled space. However, it is customary with other porous systems to use a different classification which depends on how water behaves in the pores. Micropores are considered to form the intrinsic porosity although there are good reasons to include also the smaller mesopores. Both meso and macropores make up the capillary pore system.

In cement paste these pores form a continuum which can be measured using mercury intrusion porosity (MIP) down to the largest of gel pores (small mesopores). Sorption techniques are required to investigate the finest mesopores and micropores. Both capillary pore volume and pore size decrease significantly as hydration proceeds, or as w/c ratio is reduced. MIP is the most useful method of measuring pores for permeability predictions, but it must be remembered that there are several important assumptions inherent in the calculations and we are not

really measuring absolute values. This will become clearer in later discussion.

CAPILLARY FLOW

Flow in capillary pores can be described by D'Arcy's law for laminar flow through porous media:

$$dq/dt = KA(\Delta h/L)$$
(1)

where dq/dt is the rate of flow, A is the cross-sectional area of the specimen, and $\Delta h/L$ is the hydraulic gradient across the section. K is the measured proportionality constant which represents the ease with which water flows through the specimen. The permeability coefficient is a material constant independent of the fluid used:

$$K' = \frac{K\eta}{\rho g}$$
(2)

where η is the viscosity of the fluid, ρ is its density, and g is the gravitational constant. In practice the measured value K is usually reported as the permeability coefficient, rather than K'. The first comprehensive study of the factors affecting permeability of cement paste using this approach was made by Powers and his co-workers [2,3]. They quantitatively showed the effects of w/c ratio (Figure 2) and time of moist curing (Table It was shown that well-cured pastes can attain very low 1). permeabilities, characteristic of dense rocks, even though the total pore volumes of these pastes are high (Table 2). This was attributed to the fact that the continuous capillary pore system, through which water flows relatively easily, becomes cut off by the deposition of hydration products. The time at which this can occur is strongly dependant on the w/c ratio of the paste (Table 3).

In such discontinuous pore systems flow is limited by movement through the very fine gel pores (micropores), so that D'Arcy flow is greatly modified by the adsorption of water on the pore surfaces. Powers <u>et al</u>. [4] developed a theoretical approach to model this using Stokes Law applied to a concentrated suspension. Equation 3 was derived using a number of simplifying assumptions, which gave good agreement between observed and calculated values over the range $0-30^{\circ}C$.

$$K_{1} = \frac{1.36 \times 10^{-12}}{\eta(\Theta)} \frac{(1-c)^{2}}{c} \exp(-\frac{1242}{T}) + 0.7(\frac{c}{1-c})$$
(3)

where $\eta(\Theta)$ is the viscosity of the fluid as a function of temperature T, and c is the volume fraction of solid material. (The porosity of the paste is equal to (1 - c) - 0.26). However, since in practice permeation in concrete mostly involves capillary flow, we will not concern ourselves with the details of this approach.

Hughes [5] used a different approach, considering Poisueille flow in a 3-D random array of tortuous porcs with circular cross-section. The flow equation thus obtained is:

$$dq/dt = \left(\frac{P}{32n^2\eta}\right) r^2 A(\Delta h/L)$$
(4)

where P is the porosity, n^2 is a tortuosity factor, and r is the pore radius.

INFLUENCE OF PORE STRUCTURE

Since the work of Powers, MIP has been developed commercially, so that pore size distributions can be measured routinely. Briefly, the method measures the volume of mercury forced into the pores under an applied pressure. Pore size is related to pressure by the Washburn equation, which assumes a circular cross section

$$P = -\frac{2\gamma\cos\theta}{r}$$
(5)

where γ is the surface tension of mercury and θ is the contact angle. In recent years there have been attempts to correlate pore structure with permeability. Parameters used and defined for this purpose are given in Figure 3. The pore diameters used to limit V₁ and V₂ are arbitrary and several values have been used: 135nm [6], 88nm [7], 75nm [8], and 50nm [5] for V₁; 30nm [6] and 15nm [5] for V₂.

Using paste of different w/c ratios Mehta and Manmohan [6] obtained extensive data, part of which is summarized in Table 4, from which the Equation 6 was obtained by regression analysis

$$\ln K = 3.84V_1 + 0.20V_2 + 0.56 \times 10^{-6} d_t + 8.09V'_t - 2.53 \text{ m/s}$$
(6)

where V'_t is the total capillary porosity divided by the degree of hydration [i.e., $V'_t = (V_1 + V_2)/\alpha$]. This accounts for different amounts of hydration. Inspection of Equation 6 shows that V_1 and V'_t are the most important parameters and the porestructure-permeability relationship can be approximated by:

$$\ln K = 4V_1 + 8V'_t - 2.5 \text{ m/s}$$
(7)

or by [8]:

$$\ln K = 10.9V_{\rm t}' - 3.4 \tag{8}$$

Nyame and Illston [9], on the other hand, found a good correlation between ln K and ln r_{∞} (Figure 4). This latter parameter was taken to represent the smallest radius for which there is a continuous capillary pore system through which D'Arcy flow can

occur. A similar correlation with threshold diameter could be obtained [6] with a similar justification. In this way the complications of flow through micropores is eliminated from the analysis.

Hughes [5] used Equation 4 together with MIP data to obtain an experimental function for r^2 . A value of 2.5 was used for n^2 , which has been estimated for fluid flow through granular beds [10]. Hughes also recognized the restrictive nature of the gel pores, which were eliminated in the analysis by ignoring all pores with r < 7.5 mm. He also assumed that he was considering only the continuous pore system (as suggested by Nyame and Illston) by using the <u>second</u> intrusion curve (Figure 5). The first intrusion is considered to fill all capillary pores, but only those pores without restricted entryways will empty during extrusion. Thus the second intrusion is a measure of the continuous pore system through which mercury flows readily, and presumably also water.

Effect of Curing Temperature

The pore size distribution is strongly influenced by the curing temperature: high temperatures increase the volume of large mesopores [8,11] (see, for example Figure 6). One might expect this change to be reflected by higher permeabilities, and this has indeed been found [8,12] when curing temperatures are varied (see control curves in Figure 7).

Effect of Drying

The early work at PCA showed that drying a well-cured paste increased the K value nearly 100-fold [2]. Recent studies have shown that drying changes the pore size distribution [13,14], being most graphically illustrated by observing freezing behavior [14] (see Figure 8).

Effect of Mineral Admixtures

Mineral admixtures, such as fly ashes and slags, are now accepted as valuable ingredients for durable concrete. Reductions in permeability are believed to be an important aspect of their beneficial effects. Several studies [7,15,16] have shown that for cement pastes containing reactive mineral admixtures, such as fly ash, silica fume, and rice husk ash, the total porosity is reduced compared to pastes of pure cement and a finer pore structure results (Figures 9 and 10). These changes correlate qualitatively with observed reductions in permeability. However, pastes containing fly ash show anomalous behavior. Such pastes have reduced permeabilities even though the much slower reactions of fly ash result in higher porosities and coarser pore structures even after 60 days curing (Figure 9).

It is clear that the pore structure-permeability relationships discussed above do not apply here. The pozzolanic

reaction seems to be able to develop a discontinuous pore system more readily [17]. Recently Feldman [18] has concluded that pastes containing fly ash are more prone to damage when MIP is used to measure pore sizes. This can be seen by comparing the first and second intrusion curves (Figure 4). It appears that mercury under pressure breaks through rather fragile barriers that isolate large pores, whereas this does not happen in pure cement pastes. These results suggest that lack of adequate curing of concretes with fly ash could seriously affect its potential permeability. However, increased curing temperature greatly increases the rate of pozzolanic reaction and reduces water flow [12] (see Figure 7). In contrast the curing temperature had a much less effect on slag hydration.

The pronounced reduction in pore size in pastes containing silica fume is attributed [16] both to its high pozzolanic reactivity, and also to its very small particle size which allows it to pack efficiently between the cement grains, thereby subdividing the space. The permeability coefficients are thus greatly reduced [18], particularly at high w/c ratios (Table 5).

Effect_of Chemical Admixtures

Chemical admixtures should also affect permeability if they change pore size distributions in cement pastes. Additions of calcium chloride increase the volume of fine capillary pores at the expense of large ones [15,20] and provide a less permeable paste [15]. The addition of water-reducing agents should reduce permeability if they are used to lower w/c ratios. However, like calcium chloride, water reducing agents often increase drying shrinkage, which has been correlated with finer pores. Thus, they may well reduce permeability even when the w/c is not A more uniform dispersion of cement grains within a changed. paste, which is a consequence of using a water reducing agent, is more likely to provide a more uniform pore structure with less coarse pores.

Mortars and Concretes

It is now well known that the cement-aggregate interface is more porous than the bulk paste, in all but very well-cured systems [21]. This has been demonstrated by SEM observations, but it is not so easy to quantify. Only a few comparative MIP measurements on paste and mortars have been made [22,23] see Figure 11. It seems likely that the interfacial zone will be a favorable pathway for water flow. This is even more likely if bond cracking occurs under local stresses caused by thermal mismatch between paste and aggregate, or restraint of paste shrinkage by the aggregate.

The permeability coefficients for concrete are generally about 100 times higher than for comparable pastes (Figure 12) while for mortars they are 3-10 times higher.

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CONCLUDING DISCUSSION

A link between pore structure and permeability has now been clearly established for cement pastes, although the exact quantitative relationships still need to be refined. It should be possible to meld the various approaches into a unified theory. Specific relationships need to be developed for pastes formed with blended cements, taking into account the anomalies inherent in the measurements. The role of the cement-aggregate interface needs to be further studied and quantified if the performance of field concrete is to be predicted with certainty.

Two cautionary notes should be mentioned which merit further consideration. Space does not permit detailed discussions; either topic could well be the subject of a separate paper. The first concern involves the assumptions inherent in the porosimetry measurements. Analysis involves idealized assumptions of geometry which are not realistic; the problem of restricted entryways to large pores is particularly trouble-Furthermore, the paste or mortar must be strongly dried some. before mercury can be intruded. It is now recognized that drying significantly changes the pore structure (see Figure 8), particularly in pastes with a fine pore structure. Also. internal shrinkage stresses in mortars or concretes associated differential shrinkage of paste and with aggregate will undoubtedly lead to the formation of microcracks. It is uncertain the degree to which the apparent pore structure determined experimentally differs from the original material under study. Direct pore structure measurements on undried specimens would be most desirable.

The second concern is the degree to which the permeability coefficient for a given paste or mortar will differ for different chemical species, i.e., water, chloride ions, sulfate ions and mercury (in porosimetry). Until such relationships are known the prediction of field concrete durability from laboratory data cannot be successful. Accurate laboratory measurements of permeability coefficients require experiments of long duration with inherently large scatter. Current approaches to in situ permeability measurements need to be critically examined, and a continued search maintained for alternate methods.

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TABLE 1

Time of Curing (Days)	Permeability Coefficient (m/s)
1	10-8
3	10-9
7	10-11
14	10-12
28	10-13
90	10-16

Effect of Curing Time of Cement Paste (w/c = 0.51) on Its Permeability Coefficient (Based on Data from Ref. 2)

TABLE 2

Comparisons of Permeability and Capillary Porosity between Well-Hydrated Cement Paste and Natural Rocks (Data from Ref. 2)

Rock		Permeability	Cement Paste		
Туре	Porosity (%)	Coefficient (m/s)	Porosity (%)	wc	
Sandstone	4.3	1.7 x 10 ⁻¹¹	30	0.71	
Limestone	3.1	8.0 x 10 ⁻¹³	28	0.66	
Fine-graine Marble	ed 1.8	3.3 x 10 ⁻¹⁴	15	0.48	
Dense Trap	0.6	3.5 x 10 ⁻¹⁵	6	0.38	