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COMPARISON OF MEASURED AND CALCULATED PERMEABILITIES FOR HARDENED CEMENT PASTES

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ABSTRACT

The experimental and calculated permeabilities of hardened cement pastes were compared. Experimental data for water permeability was obtained from the work of Nyame and Illston in 1980 on neat pastes with water-to-cement ratios (w/c) between 0.23 and 1.0. Mercury intrusion porosimetry (MIP) and impedance spectroscopy (IS) measurements were performed on equivalently prepared specimens. Then the Katz-Thompson relation was used to calculate permeability. Calculated results track well with experimental data as a function of time, with the experimental value of permeability slightly higher at most times. The correlation between experimental and calculated permeabilities, at all times, are within 1.5 orders of magnitude. The largest differences occurred at late times for the samples with low w/c ratio. This calculated permeability is quick, relatively simple and appears to give reasonable results when compared to conventional water intrusion methods.

Introduction

Durability is an important practical property when designing most cement-based structures. One method of estimating the durability of a porous material is by measuring the rate at which a fluid, gas or liquid, permeates through the material under a given head of pressure. The more quickly a fluid moves through the material, i.e. higher permeability, the lower the anticipated durability. Similarly, if a fluid moves through the material at a very slow rate, i.e. low permeability, a high durability would be expected. Performing a permeability measurement also makes it possible to attach a number to the durability of a sample, something which may otherwise be characterized somewhat subjectively by standard durability tests.

There have been a number of studies on the permeability of both concretes and mortars [1-3], as well as pastes [4-13]. Liquid or gaseous water is generally used as the penetrant fluid, though results from experiments using oxygen or nitrogen gas have been reported [2,

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14]. Also, the rate that the pore water exchanges with an organic solvent has been used as a means of estimating the relative permeability of cement-based materials [2]. Despite the use of a wide range of sample configurations, test apparati, penetrant fluids, etc., these studies have shown that the permeability of a cement paste or concrete can be decreased with three primary methods: (1) by decreasing the initial water to cement ratio of the mix, (2) by increasing the degree of hydration, and (3) by adding pozzolanic materials, such as flyash, blastfurnace slag, or silica fume.

It is apparent from the wide range of methods used to assess the permeability of cement-based materials that it is a difficult experiment to perform. High pressure measurements can take weeks to reach steady-state and may introduce flaws into the material. Also, continued hydration during testing of young specimens can result in erroneous results. The experimental apparatus can be very detailed and costly, and, in spite of this, the results are often specific to a particular apparatus and cannot be compared amongst various laboratories. Hooton [14-15] has discussed many of these problems at length.

Another problem is with the detection threshold. The fluid must penetrate through the material and the flow rate must be measured with reasonable accuracy. However, some high performance materials have been produced with properties that are difficult to assess, i.e. no fluid penetrates within a "reasonable" period of time. Mature cement-based materials have relatively low permeabilities ($< 10^{-13}$ m/s) initially; the measurement is further complicated by the addition of supplementary cementing materials, i.e. pozzolans, which reduce the permeability to an almost immeasurably low level. Therefore, it would be useful to have a fundamental way of evaluating the permeability of a material, even when it is difficult to measure a flow rate.

A number of theoretical approaches are discussed in the literature [16-20], including a critical review on theories given by Garboczi [21]. D'Arcy's law and the Kozeny-Carmen equation are the most discussed and popular theoretical approaches. However, both lack some useful properties. For example, to apply D'Arcy's law, it is necessary to reach a steady-state flow, something that is often difficult to achieve. To apply the Kozeny-Carmen equation, one must have an accurate measurement of the surface area relevant to flow. This is difficult to obtain because cement paste contains a substantial portion of fine-scale porosity (gel surface area) which does not contribute strongly to transport, hence the "relevant" surface area is often over-estimated. Schwartz and coworkers [22] have also derived a relationship to predict permeability for porous materials which employs a delta parameter, in contrast to a characteristic length scale.

The approach discussed in this paper is that of Katz and Thompson [23]. They derived an expression for the permeability of a porous material which is sensitive to the scale at which a fluid permeates. The permeability, $k'(m^2)$ is expressed mathematically by:

$$k' = \frac{1}{226}\frac{\sigma}{\sigma_o} l_c^2 \tag{1}$$

where σ is the electrical conductivity of the saturated porous material (S/m), σ_o is the conductivity of the solution in the pores (S/m), and l_c is the characteristic length scale of the material. Katz and Thompson [24] have shown that l_c can be generated from an MIP experiment. It corresponds to the pore diameter at the inflection point on a cumulative volume versus pressure diagram. Hence, this approach treats the permeability of a material as being controlled by two components, the "connectedness" of the pore space (σ/σ_o) and the pertinent length scale ($l_c=d_c$). Although this equation may be imperfect, they have shown that this relation works well for porous rocks, but presently only El-Dieb and Hooton [25] have comprehensively studied its application to concrete [25]. In their study, σ/σ_o was calculated from MIP data and not measured directly by electrical techniques as we have done in this study. They concluded that the Katz-Thompson relationship does not apply to concrete.

For clarity in comparing the data of various researchers, permeability in units of linear flow can be obtained from k′ using the following relation:

$$k(m/s) = k'(m^2) * \frac{\rho g}{\eta} \tag{2}$$

where ρ is density of the fluid (g/cm³), g is the acceleration of gravity (m/s²), and η is the viscosity of the fluid (P). For water at 20°C, the conversion term $\rho g/\eta$ equals 9.79×10^6 $m^{-1}s^{-1}$.

Because the pore structure of concretes is even more complex than that of neat cement pastes and it is difficult to obtain an accurate value of d_c for small samples by MIP, we have investigated only hardened cement pastes in this study. For simplicity, and because of the complex nature of permeability experiments, experimental permeability values for companion samples were gleaned from the literature. The results of Nyame and Illston [4-5] were chosen for comparison because they are from one of the few studies that are reported over a wide range of w/c ratios and hydration times.

Experimental

Samples were prepared to duplicate as closely as possible those of Nyame and Illston [4-5]. Type I portland cement (Table 1) and deionized water were used to prepare pastes at water-to-cement ratios (w/c) of 0.23, 0.47, 0.71 and 1.00. Pastes were mixed in a planetary mixer for 5 minutes before casting into 5cm × 15cm cylinders. Pastes with w/c = 0.71 and 1.00 were rotated for 4 hours after mixing to prevent sedimentation before casting. Two sets of samples were prepared at each w/c and were all demolded after 24 hours. The top 40% of each cylinder was cut off and discarded, leaving a sample of uniform porosity. One set was cured continuously at 100% r.h., while the other set was cured for the first 24 hours at 100% r.h., followed by curing in saturated lime water for the duration of the test. Nyame and Illston cured samples using the latter of these two methods.

TABLE 1
Composition of Type I Portland Cement Used in This Study

Raw Oxide	Wt. %	Bogue Phase	Wt. %
CaO	63.22	C_3S	54
SiO_2	20.80	C_2S	19
Al_2O_3	4.62	C_3A	9
Fe_2O_3	2.57	C_4AF	8
SO_3	2.70		
MgO	4.15	LOI	0.89
Na_2O	0.16		
K_2O	0.51		

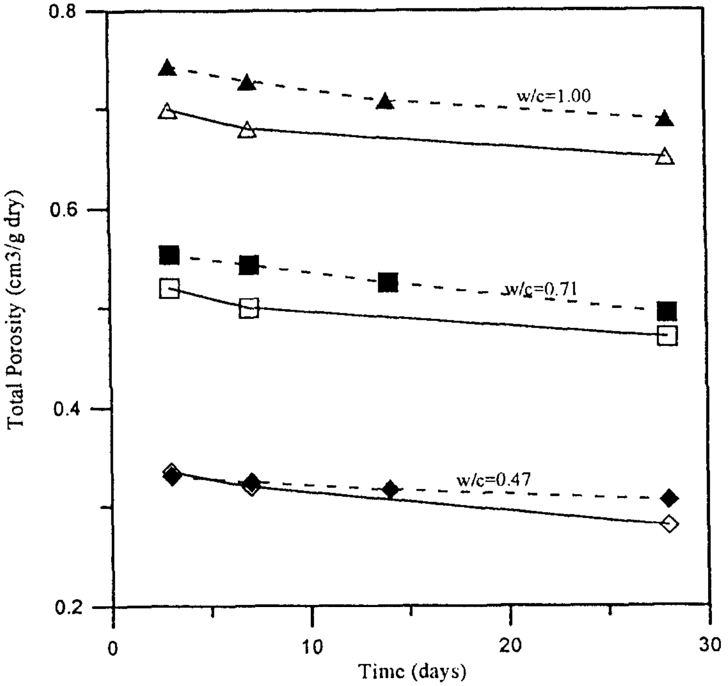

FIG. 1.

Volume fraction total porosity versus time for hardened pastes. Dotted lines (solid symbols) represent data obtained in this study; solid lines (open symbols) from Nyame and Illston [4-5].

Conductivity measurements of hardened cement pastes and pore solutions were obtained on a Hewlett-Packard 4192A impedance analyzer. The conductivity of each sample was calculated from the resistance at the point where the bulk and electrode arcs intersected (minimum imaginary value) [26]. Stainless steel electrodes were pasted to the cylindrical specimens using a thin layer of fresh paste of the same w/c ratio as the sample.

On the appropriate day, samples for mercury intrusion porosimetry (MIP) were obtained by fracturing portions of the bulk paste specimens with a hammer and collecting the shards

TABLE 2

w/c = 0.47 Pastes Cured in Saturated Lime Water

time (days)	degree of hydration	σ (S/m)	σ_0 (S/m)	d_c (μm) Nyame	d_c (μm) This study	ϕ_{cap} (calc.) (cm^3/cm^3)	ϕ_{tot} (calc.) (cm^3/cm^3)	ϕ_{tot} (meas.) (cm^3/cm^3)
1	-	-	-	-	-	-	-	-
2	0.521	-	-	-	-	0.3302	0.4699	0.4738
3	0.545	0.131	6.58	1.0	-	0.3177	0.4639	0.4641
7	0.610	0.111	5.53	0.38	0.19	0.2839	0.4475	0.4498
14	0.668	0.101	5.01	0.16	-	0.2538	0.4330	0.4402
28	0.730	0.0902	4.16	0.078	0.079	0.2216	0.4174	0.4319

TABLE 3
w/c=0.71 Pastes Cured in Saturated Lime Water

time (days)	degree of hydration	σ (S/m)	σ_o (S/m)	d_c (μm) Nyame	d_c (μm) This study	ϕ_{cap} (calc.) (cm^3/cm^3)	ϕ_{tot} (calc.) (cm^3/cm^3)	ϕ_{tot} (meas.) (cm^3/cm^3)
1	-	-	-	-	-	-	-	-
2	0.519	-	-	-	-	0.4881	0.5947	0.6074
3	0.549	0.265	2.19	2.2	-	0.4762	0.5890	0.6035
7	0.590	0.198	1.93	0.8	0.96	0.4600	0.5810	0.5889
14	0.661	0.157	1.45	0.3	-	0.4318	0.5674	0.5698
28	0.767	0.148	1.71	0.2	0.33	0.3896	0.5471	0.5572

which were nearly spherical and had diameters close to 1 cm. Five to ten of these fragments were immersed in 50 mL containers of isopropyl alcohol (IPA) for 48 hours, replacing with fresh IPA after 24 hours. Subsequently, fragments were removed from the IPA and dried by pumping under a 10^{-5} Torr vacuum for 24 hours. This was followed by 2 hours of oven-drying at 105°C. Samples were moved directly from the oven to a desiccator containing calcium sulfate desiccant and remained there until testing. MIP experiments were performed using a Quantachrome Autoscan 33 porosimeter. One to two fragments were used for the intrusion experiment. The pressure in the porosimeter was increased and decreased at a constant rate of ~130 psi/min. The pore dimension corresponding to the inflection point in the cumulative intruded-versus-pressure plot (maximum in dV/dP vs P) was interpreted as the maximum continuous length scale (l_c). A surface tension of 480 ergs/cm^2 and a contact angle of 130° were used in the Washburn equation to convert applied pressure to pore diameter.

Pore solution was extracted from hardened cement pastes using a high-pressure die. Details of the extraction process are discussed elsewhere [26].

Porosity measurements were obtained by cutting 2mm × 50mm disks from the samples that were cured in water and then oven drying them at 105°C until a constant weight was achieved (1-2 weeks). The volume of each disk was obtained prior to drying by recording both the saturated surface dry (SSD) weight and the weight while suspended in water (Archimede's principle). Each reported porosity value (measured) represents the average of three samples. The volume fractions of capillary porosity and total porosity were also calculated from the degree of hydration using equations described elsewhere [26].

TABLE 4
w/c=1.0 Pastes Cured in Saturated Lime Water

time (days)	degree of hydration	σ (S/m)	σ_o (S/m)	d_c (μm) Nyame	d_c (μm) This study	ϕ_{cap} (calc.) (cm^3/cm^3)	ϕ_{tot} (calc.) (cm^3/cm^3)	ϕ_{tot} (meas.) (cm^3/cm^3)
1	-	-	-	-	-	-	-	-
2	0.527	-	-	-	-	0.5988	0.6831	0.6824
3	0.587	0.376	1.72	5.0	-	0.5802	0.6741	0.6791
7	0.605	0.289	1.47	3.0	2.4	0.5746	0.6714	0.6684
14	0.686	0.227	1.31	1.6	-	0.5496	0.6593	0.6620
28	0.786	0.189	1.24	0.68	0.79	0.5186	0.6443	0.6556

TABLE 5

w/c = 0.47 Pastes Cured in 100% r.h. Chamber

time (days)	degree of hydration	σ (S/m)	σ_o (S/m)
1	0.393	-	-
2	0.504	-	-
3	0.569	0.119	8.33
7	0.583	0.0990	9.09
14	0.661	0.0855	10.1
28	0.723	0.0750	10.5

Results and Discussion

Verification of Equivalence to Nyame and Illston Study. The total porosities and pore diameters obtained in this work and Nyame and Illston [4-5] were compared to verify that the samples were equivalent. Total porosity results are shown in Fig. 1. Samples prepared at w/c = 0.47 compared well, while the samples at w/c = 0.71 and 1.00 from this study were slightly higher than Nyame and Illston. Apparently the rolling and casting procedure used in this study was more effective in retaining water and preventing bleeding. MIP measurements were performed on these samples at 7 and 28 days. The maximum threshold pore diameters exhibited a similar trend and are shown in Tables 2-4. Pore diameters for the w/c = 0.71 and 1.00 pastes were similar or slightly higher than those of Nyame and Illston, while that of the w/c = 0.47 pastes were slightly lower, especially at early times. Part of this may be due to the small differences in the compositions of the cements used in the two separate studies. It was concluded that the specimens were similar enough to make meaningful comparisons.

Also included in Tables 2-4 are the degree of hydration and conductivity data as a function of time. The degree of hydration, as measured by LOI, increases with increasing hydration time, and with increasing w/c at a fixed time, as expected. The conductivity, on the other hand, is not as well-behaved. The paste conductivity decreases with increasing time and increasing w/c, as expected, but the conductivity of the pore solution decreases with time, opposite to previously observed trends [26]. Chemical analysis of the pore solution revealed that the concentration of alkalis decreased as a function of time, probably indicating that the alkali species were leaching into the curing water. Since it is likely that leaching

TABLE 6

w/c = 0.71 Pastes Cured in 100% r.h. Chamber

time (days)	degree of hydration	σ (S/m)	σ_o (S/m)
1	0.458	-	-
2	0.519	-	-
3	0.542	0.387	5.16
7	0.616	0.246	5.71
14	0.672	0.161	6.08
28	0.758	0.112	6.84

TABLE 7
w/c = 1.0 Pastes Cured in 100% r.h. Chamber

time (days)	degree of hydration	σ (S/m)	σ_o (S/m)
1	-	-	-
2	0.530	-	-
3	0.608	0.532	5.06
7	0.611	0.383	5.39
14	0.692	0.261	5.86
28	0.770	0.161	6.21

would create an ionic concentration profile along the radius of the sample, thereby resulting in a preferential conduction path for electric current along the inner core of the specimens, these data were deemed unreliable for calculating the normalized conductivity of the samples. Instead, equivalent samples were prepared and cured under 100% r.h. conditions. Conductivity and degree of hydration data obtained under these curing conditions are shown in Tables 5-7. No substantial difference in the degree of hydration under the two different curing conditions was observed, hence the pore structures of the two sets of samples were considered equal.

Permeability Comparison. It was difficult to extract pore solution at late times from the samples of w/c = 0.23, so data is not shown for this set. Permeability values obtained from both the Katz-Thompson equation, as well as the experimental values of Nyame and Illston are shown in Figure 2. For pastes of w/c = 0.47, 0.71 and 1.00, the values calculated from the Katz-Thompson equation are higher than those obtained by actual water permeability tests. At the two highest water-to-cement ratios, the trend with time is good, with an almost constant difference at all times through 28 days. At the lowest water-to-cement ratio, the deviation increases with hydration time.

There has been some discussion in the literature about the appropriate value of the constant in the Katz-Thompson equation. Schwartz and others [22, 27, 28] have modified Katz and Thompson's derivation and obtained a constant ranging from 1/26 to 1/128, depending on the shape used to define the pore space (i.e. spheres, long cylinders, etc.). Any choice of these possible modified values of the constant increases the value of the permeability calculated from the equation and would increase the discrepancy between the calculated and experimental values discussed in this paper. Nevertheless, the slope of the curves is fairly constant, indicating that the scaling with time is reasonable. Additional work is necessary to better establish a proper value for this constant.

The recent work of El-Dieb and Hooton suggests that the Katz-Thompson equation may be valid for porous rocks, but it is not accurate when applied to concrete [25]. It is important to point out that the value of σ/σ_o used in their work was calculated from MIP data using a method described by Katz and Thompson [24] and was not computed directly from electrical measurements. Similar computations of σ/σ_o from MIP data collected on these samples in our laboratory did not correlate well with values collected directly from electrical conductivity measurements. Hence, while the derivation for calculating σ/σ_o from MIP data [24] may be suspect, equation 1 still appears to have validity.

Agreement between experimental permeabilities [4, 5] and permeabilities calculated from impedance spectroscopy and MIP via the Katz-Thompson relationship [23] is within 1.5

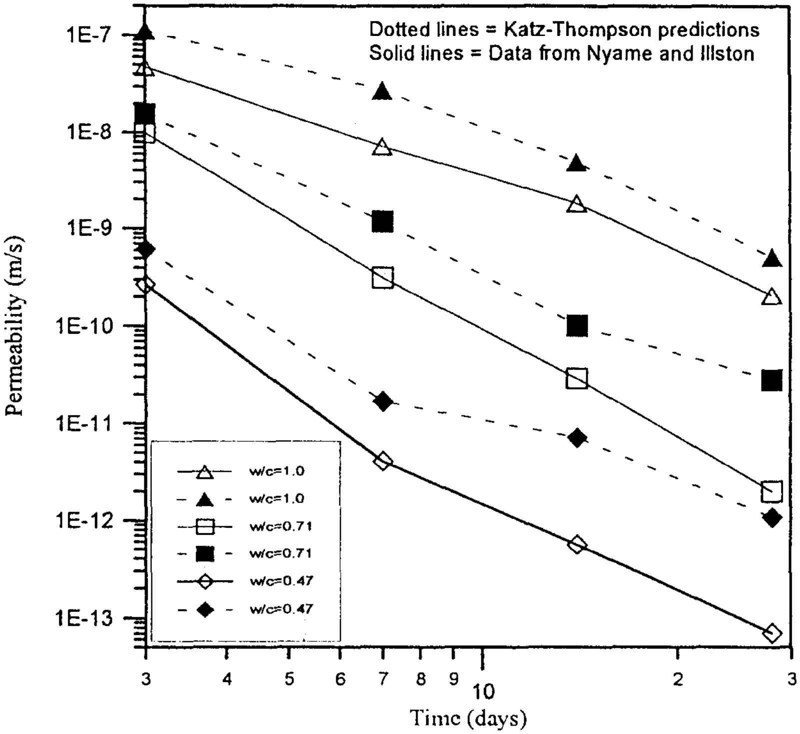

FIG. 2.

Permeability as a function of time on a log plot for data obtained from Nyame and Illston [4-5], as well as calculated from the Katz-Thompson equation [23] using MIP (d_c) and normalized conductivity (σ/σ_o) data.

orders of magnitude over 1-28 days and a range of w/c in cement pastes. To more fully establish the Katz-Thompson approach, it is desirable to perform permeability, MIP, and impedance spectroscopy measurements on identical specimens and over a longer time period. To test the general applicability of the Katz-Thompson approach, experiments on cement-based systems that contain pozzolans and aggregates should be undertaken.

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