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A NEW APPROACH TO THE DETERMINATION OF PORE DISTRIBUTION BY PENETRATING CHLORIDES INTO CONCRETE

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ABSTRACT

In this paper, a new concept of pore distribution is discussed and consequently a new approach to the determination of pore distribution by penetrating chlorides into concrete is proposed. This approach involves 1) accelerating chloride penetration into concrete specimens by applying an electrical field, 2) determining the profile of total chloride content by using the dry-grinding technique and chemical analysis, and 3) calculating the pore distribution of concrete from the profile of total chloride content. A number of specimens have been tested. Preliminary results show that the pore distributions determined by using the new approach are qualitatively comparable with those determined by using conventional mercury intrusion technique.

Introduction

The pore structures of concrete strongly affect its properties, especially its transport properties, such as permeability and diffusivity. Many studies have been carried out in order to find the relationships between the transport properties and pore size distribution of cement based materials. Mehta (1) proposed an empirical formula to express the relationship between permeability and pore size distribution. Tang and Nilsson (2) modified Hagen-Poiseuille's formula by introducing a resistant force imposed by pore surface, and derived a quantitative relationship between permeability and pore size distribution of cement pastes. The calculated permeability agrees well with the measured value. Garboczi (3) advocated an application of the Katz-Thompson theory for predicting the permeability of cement paste from its pore structure. Recently Halamickova et al (4) examined the application of the Katz-Thompson theory and found that the theory works well when w/c > 0.4, whereas EL-Dieb and Hooton (5) concluded from their evaluation that the Katz-Thompson theory was not successful for cement and concrete data.

So far, studies on the relationships between transport properties and pore structure are mainly confined to cement pastes, and only a few (6) relate to concrete—the final material used in practice. One of the most important reasons is the lack of methods for determining pore size distribution of concrete. Conventional methods include mercury intrusion and desorption isotherms. Due to the dynamic hesitation of mercury in pore paths, the mercury intrusion technique can be used only for very small sample sizes, normally less than 10 mm, such as paste or mortar with fine aggregate. Since concrete in practice contains aggregate of size larger than 10 mm, it is rather difficult to take a representative sample for the application of mercury intrusion technique. The desorption isotherm technique is not only time-consuming but also limited to a very small range of pores (<30 nm). It is essential to find an applicable method for determining the pore structure of concrete.

A New Approach

A new concept of pore distribution

Traditionally, pore distribution denotes the distribution of pore content to pore size. Pore size is generally referred to the radius or diameter of cylindrical pores. Unfortunately, the pore system in cement based materials is too complex to be described by using a simple model, for instance the cylindrical pore model. The pore size distribution from the mercury intrusion technique is, in fact, a plot of pore content versus mercury pressure, and the pore size distribution from a desorption isotherm is just a plot of pore content versus vapor pressure. So called pore size, e.g. radius or diameter, is just imagined under the assumption of a simple model. This might be the reason why it is difficult to find the quantitative relationships between transport properties and pore size distribution.

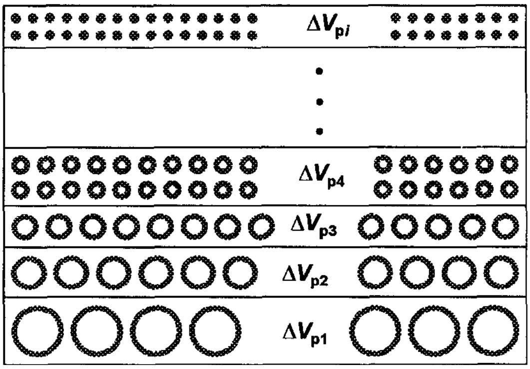


FIG. 1
Model of parallel porous bodies.

For practical purposes, it might be better to describe a pore structure by using the distribution of pore content to a transport property, instead of imagined pore size. Therefore, we suggest a model of parallel porous bodies, that is, a porous material made up of many parallel porous bodies, as shown in Fig 1. It should be noted that: 1) a porous body is here defined as a group of pores which have a certain transport property regardless of their actual shapes and sizes; and 2) the word "parallel" here does not mean a really parallel connection among porous bodies but just classifies the pores having the same transport property as a group. The rate of fluid flow in each porous body makes its contribution to the total flow. In this study, it means that the chloride diffusivity in each porous body may be different. The more porous and less tortuous a porous body, the larger the diffusivity.

Total chloride content

It is not so difficult to determine total chloride content in concrete (7-9). Total chloride consists of two parts, free chloride and bound chloride:

$$c_{\text{total}} = c_{\text{free}} + c_{\text{bound}} \tag{1}$$

Usually, c_{total} and c_{bound} are expressed in mg(Cl)/g(cement), or mg(Cl)/g(binder), and c_{free} is expressed in mol/l. To have the same unit, we rewrite Eq.(1) into

$$c_{\text{total}} = 35.45 c_{\text{free}} \left(1/f_{\text{c}} + W_{\text{n}}^{0}\, \alpha \right) \cdot V_{\text{p}} + c_{\text{bound}} \qquad \text{mg(Cl)/g(binder)} \tag{2}$$

where: W_{n}^{0} : non-evaporable water, assuming $W_{\text{n}}^{0} = 0.25$ for $\alpha = 1$;
α: degree of hydration;
V_{p} : pore content in dry concrete sample, ml/g(sample);
f_{c} : cement content in concrete by weight,

$$f_{\text{c}} = \frac{W_{\text{cement}}}{W_{\text{cement}} + W_{\text{aggregates}}} \tag{3}$$

Bound chloride can be estimated by Freundlich's law (10):

$$\begin{aligned} c_{\text{bound}} &= f_{\text{a}} c_{\text{free}}^{\ B} && \text{mg(Cl) / g(gel)} \\ &= \left(1 + W_{\text{n}}^{0}\right) \alpha\, f_{\text{a}} c_{\text{free}}^{\ B} && \text{mg(Cl) / g(binder)} \end{aligned} \tag{4}$$

where f_{a} and B are the adsorption constants. According to our early study (10), for ordinary Portland cement, $f_{\text{a}} = 10^{1.14}$ and $B = 0.379$. Total chloride content can, therefore, be expressed as

$$c_{\text{total}} = 35.45 c_{\text{free}} \left(1/f_{\text{c}} + W_{\text{n}}^{0}\, \alpha \right) \cdot V_{\text{p}} + \left(1 + W_{\text{n}}^{0}\right) \alpha\, f_{\text{a}} c_{\text{free}}^{\ B} \quad \text{mg(Cl)/g(binder)} \tag{5}$$

Relationship between pore content and total chloride content

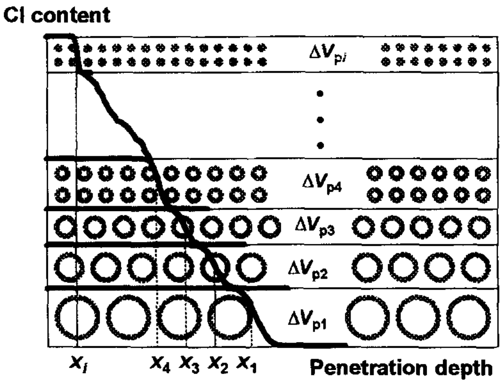


FIG. 2
Chloride penetration into different porous bodies.

As we have described previously (11), an electrical field can accelerate the penetration of chlorides into the porous bodies. Owing to the different diffusivity, the rate of chloride flow through each porous body is different, which results in different penetration depths at a certain test duration, as shown in FIG. 2. Since every chloride-contaminated porous body has approximately the same free chloride concentration and chloride binding capacity, it can be seen from Eq. (5) that the total chloride content in each porous body should be proportional to its pore content.

$$\frac{\Delta c_{\text{total}\,1}}{\Delta V_{\text{p}1}} = \frac{\Delta c_{\text{total}\,2}}{\Delta V_{\text{p}2}} = \cdots = \frac{\Delta c_{\text{total}\,i}}{\Delta V_{\text{p}i}} = \cdots = \frac{c_{\text{total}}}{V_{\text{p}}} \tag{6}$$

This implies that the pore content in a specified porous body can be estimated from the change of total chloride content between two penetration depths,

$$\Delta V_{\mathrm{p}i} = \Delta c_{\mathrm{total}i} \frac{V_{\mathrm{p}}}{c_{\mathrm{total}}} \tag{7}$$

Here V_{p} refers to the total pore content and can be determined by water saturation method, and c_{total} is the total chloride content in a fully saturated condition and can be determined experimentally or estimated by using Eq. (5).

Distribution of pore content to the reduction degree of diffusion

According to the relationship between diffusivity and penetration front (11), the diffusivity D_i in the i-th porous body can be calculated by using the following equation:

$$D_i = \frac{RTL}{zFU} \cdot \frac{x_i}{t} \tag{8}$$

where R: gas constant, $R = 8.314$ J/(K·mol);
T: solution temperature, K;
L: thickness of the specimen, m;
z: absolute value of ion valence, for chloride ions, $z = 1$;
F: Faraday constant, $F = 9.648 \times 10^4$ J/(V·mol);
U: absolute value of potential difference, V;
x_i: average penetration front in the i-th porous body , m;
t: test duration, sec.

Let

$$f_i = \frac{D_i}{D_0} \tag{9}$$

where D_0 is the diffusivity of chloride ions in a bulk solution, $D_0 = 2.03 \times 10^{-9}$ m^2/s (12). f_i can be called the reduced degree of diffusion. It is the reverse of the formation factor for the pores and includes "all the interesting features of the pore structure" (3). Therefore, f_i reflects not only pore size but also the tortuosity of a porous body. Similar to traditional pore size distribution curves, a plot of pore content V_{p} versus f could be related to an integral pore distribution and a plot of $\frac{\Delta V_{\mathrm{p}}}{\Delta \log f}$ versus f related to a differential pore distribution.

Experimental procedures

The similar experimental arrangement and procedures (11) for rapid penetration of chlorides into a concrete specimen are used in this study.

After the penetration of chlorides, pulverized samples are taken from the specimen at different depths by using the dry-grinding technique, i.e. dry-grinding on a lathe with a diamond tool, gradually from the surface exposed to a chloride solution to a certain depth. The pulverized samples are immediately dried at 105 °C and stored in a desiccator to avoid excessive carbonation.

The total chloride content in each sample is determined in accordance with AASHTO T260 (8), by using potentiometric titration with a chloride ion selective electrode and a silver nitrate solution. It has been found (9) that this analysis procedure can detect all chloride ions in concrete if enough nitric acid is added to digest the sample.

After the titration of chloride ions, the same sample solution is used for the determination of calcium content, so that the binder content in the sample can be estimated. The detailed procedures were previously reported elsewhere (13).

With the help of Eq. (7) and (9), a profile of total chloride content can be easily transformed into an integral pore distribution or a differential pore distribution.

Preliminary Tests and Discussion

Some paste and concrete specimens were used for preliminary tests. The measured profiles of chloride content are shown in FIG. 3, the pore distributions measured by using mercury intrusion technique are shown in FIG. 4, and other data concerned are listed in TABLE 1.

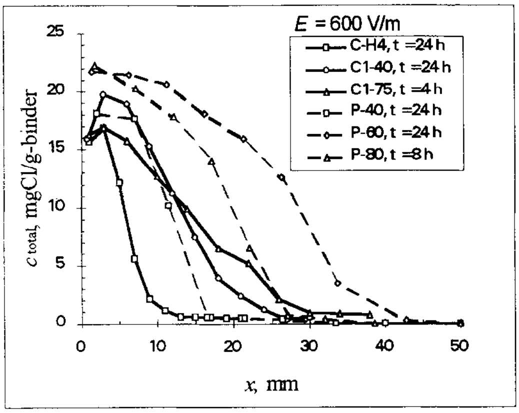


FIG. 3
Profiles of total chloride content
after CTH test.

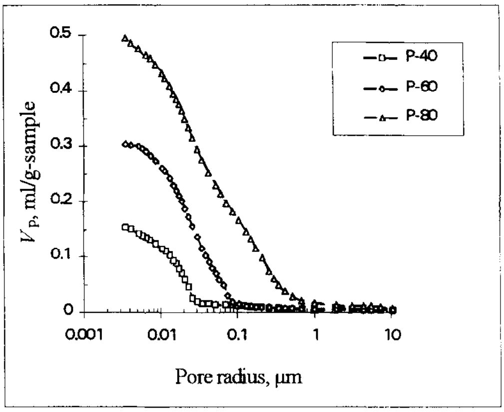


FIG. 4
Pore size distributions
from mercury intrusion technique.

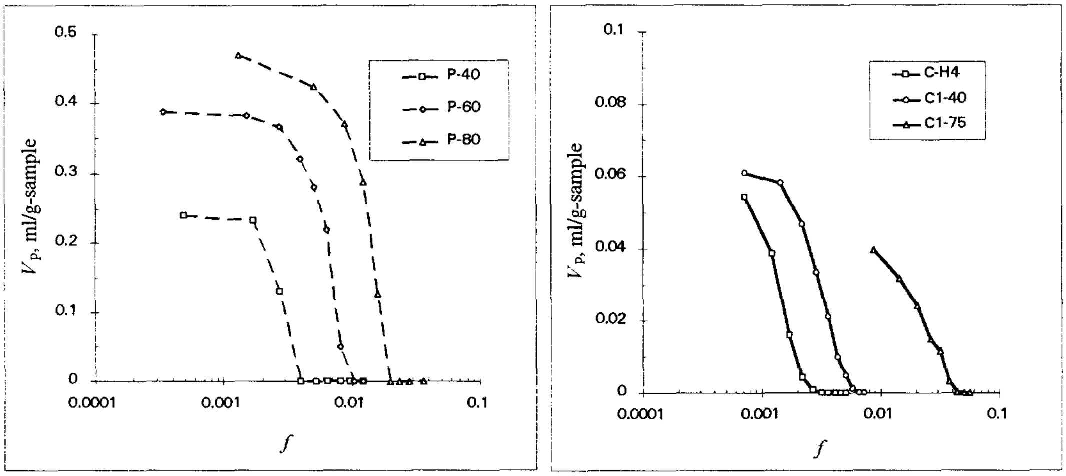
It can be seen from FIG. 3 that in some chloride profiles the chloride content in the surface layer is slightly lower than inside. One possible reason might be that the chloride binding capacity in the surface layer is lower than inside due to a big change in the chemical composition of the pore solution. These low points were not included in the calculation of pore content.

TABLE 1
Data concerned in the calculation.

Specimen No.	Binder	w/c	f_c	Age month	α	V_p ml/g(dry sample)
H4	OPC+5%CSF	0.40	0.200	12	0.8*	0.063
C1-40	OPC	0.40	0.199	46	0.9*	0.059
C1-75	OPC	0.75	0.117	12	0.9*	0.061
P-40	OPC	0.40	1	3	0.63	0.241
P-60	OPC	0.60	1	3	0.76	0.395
P-80	OPC	0.80	1	3	0.79	0.534

* estimated according to the age.

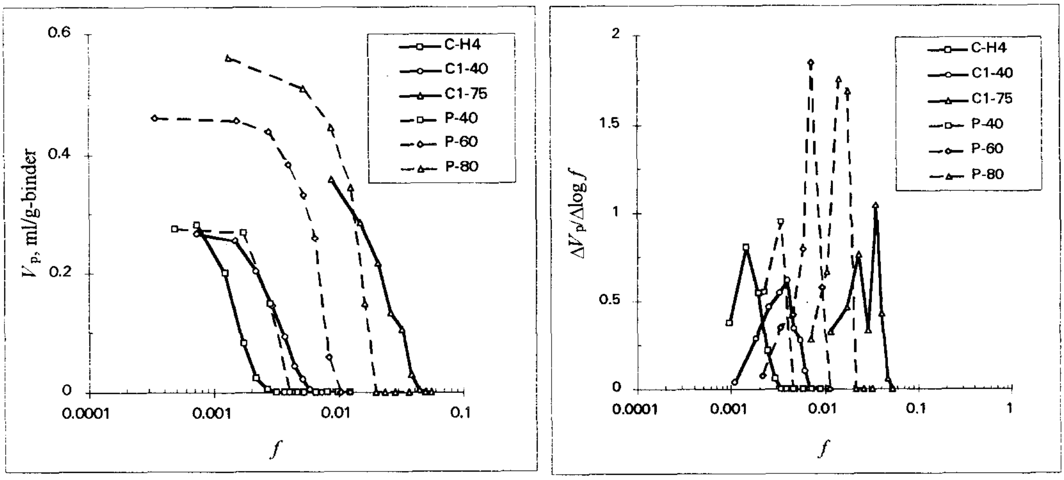
The calculated pore distributions are shown in FIG. 5. It is found that for most of the specimens tested, the calculated total pore content is very close to the measured value (ref. TABLE 1). For the specimens with high water-cement ratios, the calculated total pore content appears lower than the measured value, probably due to a short test duration which is not enough to have chlorides penetrate into small porous bodies.



a) paste specimens b) concrete specimens

FIG. 5
Pore distributions from the new method.

It can be seen that the pore distributions of cement pastes in FIG. 5 are qualitatively comparable with those in FIG. 4, except that the former show narrower and sharper distributions than the latter.



a) integral curves b) differential curves

FIG 6
Pore distributions in unit weight of binder.

In order to compare the pore distributions between paste and concrete, the pore content can be expressed in unit weight of binder, as shown in FIG. 6. It seems that the pore structure of concrete is slightly coarser than that of paste, especially for the specimen with a high water-cement ratio, in agreement with Winslow and Liu's findings (6). The concrete blended with silica fume (Specimen H4) exhibits a fine pore structure.

Concluding Remarks

The new approach proposed in this paper involves 1) accelerating chloride penetration into concrete specimens by applying an electrical field, 2) determining the profile of total chloride content by using the dry-grinding technique and chemical analysis, and 3) calculating the pore distribution of concrete by using Eq. (7) and (9).

A number of specimens have been tested. Preliminary results show that the pore distributions determined by using the new approach are qualitatively comparable with those determined by using conventional mercury intrusion technique.

Because this new method has no limitation on the size of samples, it provides a tool for determining pore distributions of concrete. The other advantages of the new method include: 1) simpler and cheaper experimental set-up than mercury intrusion porosimeter; 2) the use in tests of chemicals much less harmful than mercury; and 3) more practical parameter f involved in a pore distribution than pore radius.

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