NATIONAL BUREAU OF STANDARDS REPORT

3186

A METHOD FOR DETERMINING

THE

DIFFUSION COEFFICIENT OF A POROUS MATERIAL

by

Samuel M. Genensky

U. S. DEPARTMENT OF COMMERCE

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Abstract

A mathematical analysis based upon Fick's law is developed for a spherical body exposed to an atmosphere with a time invariant moisture concentration. An analytic solution is obtained from which diffusion coefficients may be computed.

1. INTRODUCTION

The fire endurance of many structures is greatly dependent on the amount of water adsorbed on the surface and within the capillary pores of the material of which the structure is formed. This moisture content is a function of both the pore structure of the material, its afinity for water and the moisture vapor pressure present in the ambient atmosphere within which the specimen is conditioned. Many studies have been made of the equilibrium moisture content of woods and textile fibers, as well as portland cement pastes. However, little work appears to have been done on concrete and as a result it seems worth while to perform a few exploratory tests on representative concrete specimens for the purpose of obtaining some indication of the moisture content of concretes prepared in the same fashion and dried to equilibrium under controlled ambient conditions. In planning these experiments it appeared that by proper selection of specimen shape and method of test, it would be possible to obtain moisture diffusion coefficients with very little additional effort. The present report outlines the mathematical reasoning which appears to justify this phase of the proposed work.

2. ASSUMPTIONS

It was proposed that the experiments would permit the measurement or calculation of the following for the specimen under examination:

W_o the weight of the specimen when completely dry

W_1 the equilibrium weight of the specimen exposed to an atmosphere containing moisture at a constant concentration C_0.

$W_2(t)$ the weight of the specimen, a function of time t, exposed to an atmosphere containing moisture at a constant concentration C_1. $W_1 = W_2(t_0)$, t_0 being the time the specimen is first exposed to this atmosphere.

$W_2 = W_2(t)$ $t \geq T$ the equilibrium weight of the specimen exposed to the atmosphere containing moisture at a constant concentration C_1. T is the time at which an increase in the specimen's weight can no longer be detected by the experimental apparatus.

A mathematical model based upon Fick's law which utilizes this information to obtain an estimate of the diffusion coefficient is available for a spherical specimen of radius R, throughout which the concentration of the moisture depends upon the radial distance from the center of the specimen and upon the time that the specimen has been exposed to the atmosphere containing moisture at a constant concentration C_1. This same analysis is equally applicable to a hemispherical specimen whose flat surface is completely insulated against moisture flow because here also the concentration of the moisture in the specimen again depends upon the radial distance from the center of the specimen and upon the time. For this model the solution is one-half that for the sphere.

No attempt is made to account for heats of adsorption or desorption in the following analysis.

3. ANALYSIS

Mathematically the problem becomes:

$$\frac{1}{D}\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r} \qquad (0 < r < R,\ t > t_o) \qquad (1)$$

$$C = C_2 \qquad (0 \leq r \leq R,\ t = t_o) \qquad (2)$$

$$C = C_3 \qquad (r = R,\ t > t_o) \qquad (3)$$

$$C \neq \infty \qquad (r = 0,\ t \geq t_o) \qquad (4)$$

where r is the radial distance measured from the center of the sphere. cm.

t is the time measured from the instant the specimen is exposed to the atmosphere containing moisture at a constant concentration C_1. sec.

$C=C(r,t)$ is the concentration of the moisture in the specimen and is a function of both radial distant r and time t. gm/cm^3

D is the diffusion constant for the specimen. $cm^2/sec.$

$C_2=\dfrac{W_1-W_o}{\frac{4}{3}\pi R^3}$ C_2 is the concentration in gm/cm^3 of the moisture in the specimen when it is introduced into the atmosphere containing moisture at a constant concentration C_1.

$C_3=\dfrac{W_2-W_o}{\frac{4}{3}\pi R^3}$ C_3 is the concentration in gm/cm^3 of the moisture in the specimen when it reaches equilibrium in the atmosphere containing moisture at a constant concentration C_1.

No generality will be lost if t_o is taken equal to zero. Condition (4) guarantees that the concentration remains finite at the center of the sphere in compliance with physical requirements.

$$\text{Let} \quad V = V(r,t) = C(r,t) - C_3 \tag{5}$$

Using (5) and recalling that t_o has been set equal to zero, (1) - (4) become

$$\frac{1}{D}\frac{\partial V}{\partial t} = \frac{\partial^2 V}{\partial r^2} + \frac{2}{r}\frac{\partial V}{\partial r} \qquad (0<r<R,\ t>0) \tag{6}$$

$$V = C_2 - C_3 \qquad (0\leq r\leq R,\ t = 0) \tag{7}$$

$$V = 0 \qquad (r = R,\ t>0) \tag{8}$$

$$V \neq \infty \qquad (r = 0,\ t\geq 0) \tag{9}$$

$$\text{let} \quad V = V(r,t) = \rho(r)\tau(t) = \rho\tau \tag{10}$$

$$\text{then} \quad \frac{\partial V}{\partial t} = \rho\tau', \ \frac{\partial V}{\partial r} = \rho'\tau \quad \text{and} \quad \frac{\partial^2 V}{\partial r^2} = \rho''\tau \tag{11}$$

Substituting these expressions into (6) and multiplying the resulting expression by $1/\rho\tau$ yields:

$$\frac{1}{D}\frac{\tau'}{\tau} = \frac{\rho''}{\rho} + \frac{2}{r}\frac{\rho'}{\rho} \qquad (0<r<R,\ t>0) \tag{12}$$

Let $\frac{1}{D}\frac{\tau'}{\tau}$ equal $-\lambda^2$ where λ is real (13)

Therefore $\tau' + \lambda^2 D\tau = 0$ (14)

and thus $\tau = a e^{-\lambda^2 Dt}$ where a is an arbitrary constant (15)

Now by (13) $\frac{\rho''}{\rho} + \frac{2}{r}\frac{\rho'}{\rho} = -\lambda^2$ (16)

and thus $\rho'' + \frac{2}{r}\rho' + \lambda^2\rho = 0$ (17)

Let $S = r\rho$ (18)

Using (18), (17) becomes

$$S'' + \lambda^2 S = 0 \quad (19)$$

and thus $\rho = A\frac{\cos\lambda r}{r} + B\frac{\sin\lambda r}{r}$ where A and B are arbitrary constants (20)

Now since $\lim\limits_{r\to 0}\frac{\cos\lambda r}{r} \longrightarrow \infty$, A = 0 for otherwise (9) would be contradicted.

Thus
$$V(r,t) = Pe^{-\lambda^2 Dt}\frac{\sin\lambda r}{r} \quad \text{where } P = aB \quad (21)$$

Now in view of (8) $\sin\lambda R = 0$ (22)

and thus $\lambda = \frac{n\pi}{R}$ $n = 0, \pm 1, \pm 2, \ldots$ (23)

Therefore (21) may be written

$$V(r,t) = \sum_{n=-\infty}^{\infty} P_n e^{-\frac{\pi^2 Dt}{R^2}n^2}\frac{\sin\frac{n\pi}{R}r}{r} \quad (24)$$

$$= \sum_{n=1}^{\infty} Q_n e^{-\frac{\pi^2 Dt}{R^2}n^2}\sin\frac{n\pi r}{r} \quad \text{where } Q_n = P_n - P_{-n} \quad (25)$$

$n = 1, 2, \ldots$

Considering (7) and (25) and recalling Fourier series analysis

$$(C_2 - C_3)r = \sum_{n=1}^{\infty} Q_n \mathrm{Sin}\frac{n\pi r}{R} \tag{26}$$

and thus

$$Q_n = \frac{2}{R}\int_0^R (C_2-C_3)r\ \mathrm{Sin}\frac{n\pi r}{R}\,dr \tag{27}$$

Integrating (27)

$$Q_n = \frac{2(C_2-C_3)R}{\pi}\ \frac{(-1)^{n+1}}{n} \tag{28}$$

Thus

$$V(r,t) = \frac{2(C_2-C_3)R}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\,e^{-\frac{\pi^2 Dt}{R^2}n^2}\ \mathrm{Sin}\frac{n\pi r}{R}/r \tag{29}$$

Now the total moisture content of the sphere is found by integrating V(r,t) over the volume of the sphere. Thus

$$4\pi\int_0^R V(r,t)r^2dr = 4\pi\int_0^R \left[\bar{C}(r,t) - C_3\right]r^2dr \tag{30}$$

and

$$4\pi\int_0^R C(r,t)r^2dr = \frac{4}{3}\pi R^3C_3$$
$$+8(C_2-C_3)R\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}e^{-\frac{\pi^2 Dt}{R^2}n^2}\int_0^R r\mathrm{Sin}\frac{n\pi r}{R}\,dr \tag{31}$$

Integrating (31)

$$4\pi\int_0^R C(r,t)r^2dr = \frac{4}{3}\pi R^3C_3 + \frac{8(C_2-C_3)R^3}{\pi}\sum_{n=1}^{\infty}\frac{1}{n^2}\,e^{-\frac{\pi^2 Dt}{R^2}n^2} \tag{32}$$

and for a hemispherical specimen

$$2\pi\int_0^R C(r,t)r^2dr = \frac{2}{3}\pi R^3C_3 + \frac{4(C_2-C_3)R^3}{\pi}\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-\frac{\pi^2Dt}{R^2}n^2} \qquad (33)$$

Now

$4\pi\int_0^R C(r,t)r^2dr$ is the weight of the moisture in the specimen

at time t (where t = 0 denotes the moment the specimen is placed into the atmosphere containing moisture at a constant concentration C_1). Therefore

$$4\pi\int_0^R C(r,t)r^2dr = W_2(t) - W_o \qquad 0 \leq t < \infty \qquad (34)$$

Recalling the definitions of C_2 and C_3

$$\frac{4}{3}\pi R^3C_3 = W_2 - W_o \qquad t \geq T \qquad (35)$$

and $\frac{4}{3}\pi R^3C_2 = W_1 - W_o$ (36)

Recalling that $\sum_{n=1}^{\infty}\frac{1}{n^2} = \frac{\pi^2}{6}$ and (34)-(36), (33) becomes

$$W_2(t) - W_o = W_2 - W_o + [(W_1-W_o)-(W_2-W_o)]\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-\frac{\pi^2Dt}{R^2}n^2} \qquad (37)$$

and thus

$$\frac{W_2(t) - W_2}{W_1 - W_2} = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-\frac{\pi^2Dt}{R^2}n^2} \qquad (38)$$

Let $$f\left(\frac{\pi^2 Dt}{R^2}\right) = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\frac{\pi^2 Dt}{R^2} n^2} \qquad (39)$$

and (38) becomes

$$\frac{W_2(t) - W_2}{W_2(0) - W_2} = f\left(\frac{\pi^2 Dt}{R^2}\right) \text{ recalling that } W_1 = W_2(0). \qquad (40)$$

Since $W_2(t)$, $W_2(0)$, W_2, t and R are known, (40) can thus be solved for the diffusion coefficient D. Figure 1 which is a plot of $f\left(\frac{\pi^2 Dt}{R^2}\right)$ against $\frac{\pi^2 Dt}{R^2}$ has been included to ease the labor in the evaluation of D.

For $\frac{\pi^2 Dt}{R^2} \geq 2$

$$\frac{f\left(\frac{\pi^2 Dt}{R^2}\right) - \frac{6}{\pi^2} e^{-\frac{\pi^2 Dt}{R^2}}}{f\left(\frac{\pi^2 Dt}{R^2}\right)} < 0.001$$

and thus the simpler expression $\frac{6}{\pi^2} e^{-\frac{\pi^2 Dt}{R^2}}$ becomes a very good approximation to $f\left(\frac{\pi^2 Dt}{R^2}\right)$ over that range.

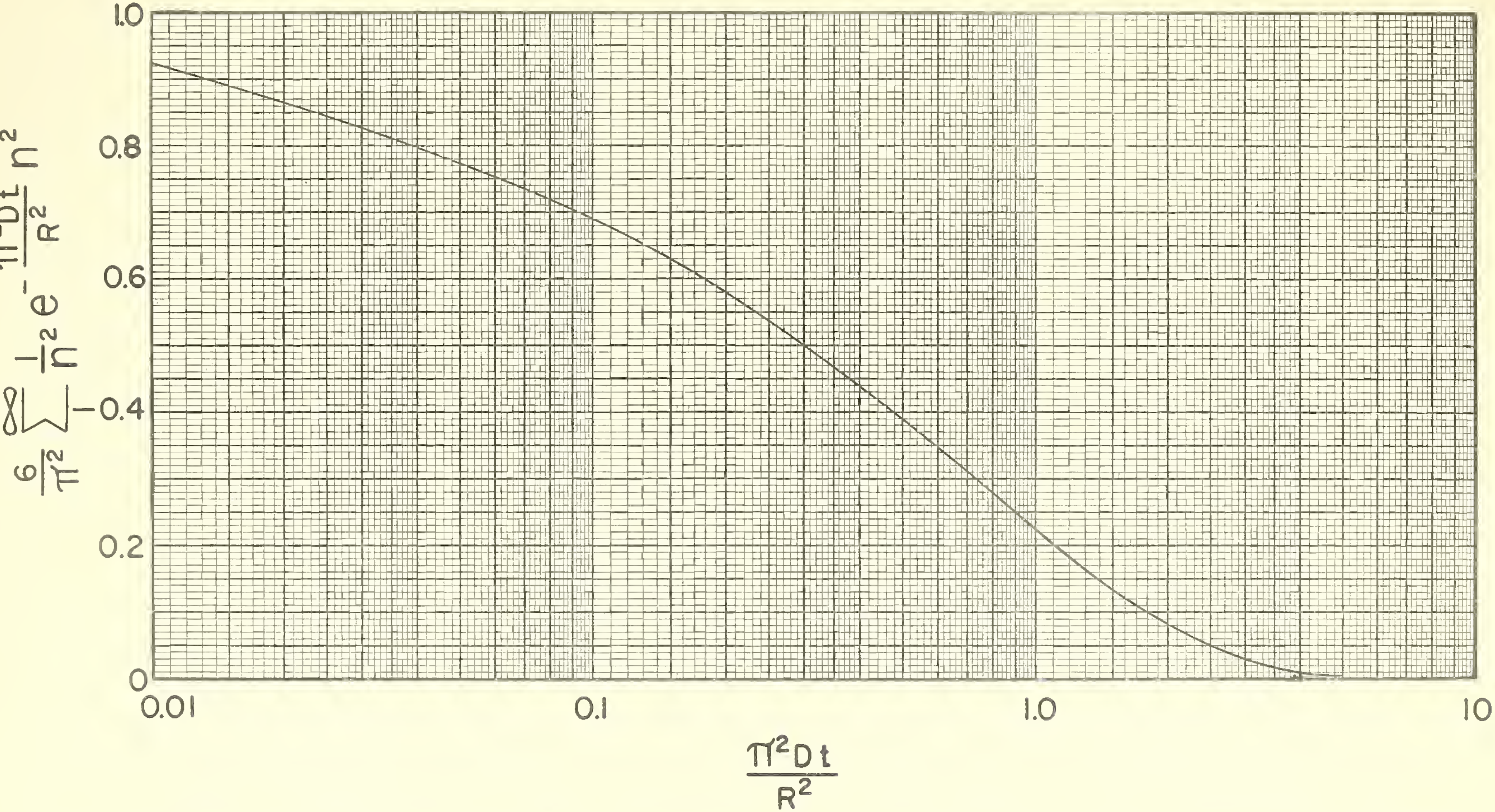

FIG. I RATIO OF UNACCOMPLISHED ABSORPTION TO TOTAL POSSIBLE ABSORPTION VS $\frac{\pi^2 Dt}{R^2}$

THE NATIONAL BUREAU OF STANDARDS

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The functions of the National Bureau of Standards are set forth in the Act of Congress, March 3, 1901, as amended by Congress in Public Law 619, 1950. These include the development and maintenance of the national standards of measurement and the provision of means and methods for making measurements consistent with these standards; the determination of physical constants and properties of materials; the development of methods and instruments for testing materials, devices, and structures; advisory services to Government Agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; and the development of standard practices, codes, and specifications. The work includes basic and applied research, development, engineering, instrumentation, testing, evaluation, calibration services, and various consultation and information services. A major portion of the Bureau's work is performed for other Government Agencies, particularly the Department of Defense and the Atomic Energy Commission. The scope of activities is suggested by the listing of divisions and sections on the inside of the front cover.

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