

Nonlinear water diffusion in nonsaturated concrete

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The equations governing drying and wetting of concrete are formulated, assuming the diffusivity and other material parameters to be dependent on pore humidity, temperature and degree of hydration. By fitting of computer solutions for slabs, cylinders and spheres against numerous test data available in the literature it is found that the diffusion coefficient decreases about 10 to 20 times when passing from 0.9 to 0.6 pore humidity. The problem is thus strongly nonlinear. Dependence on temperature is found to agree satisfactorily with the rate process theory. Effect of temperature on equilibrium pore humidity is also studied. The aging effect is defined by means of an equivalent hydration period. To enable easy prediction of drying of simple bodies, charts for the solution in terms of nondimensional variables are presented. Finally, correlation to the diffusion in a saturated concrete is discussed.

NOTATIONS

c, \bar{c} = permeability given by Eqs. (1) and (3);
 C, C_1 = diffusivity (Eqs. 8-11) and its value at $H \rightarrow 1$;
 H, H_{en}, H_s, H_{eq} = pore humidity (or relative vapor pressure), environmental humidity (Eq. 12), self-desiccation (Eq. 4), and equivalent humidity (Eq. 22);
 H_c = parameter in Eq. (20);
 J = mass flux of water (Eq. 1);
 k = inverse slope of desorption isotherm (Eq. 4);
 L = half thickness of a slab;
 n = exponent in Eq. (20);

p_l, p_v = pressure in pore water or pore vapor;
 Q, Q_h = activation energy for diffusion (Eq. 21) and for hydration (Eq. 7a);
 r = radius coordinate;
 R = radius of a cylinder or a sphere;
 t, t_e, t_0 = time, equivalent hydration period (Eq. 7) and instant of drying exposure;
 T = absolute temperature;
 w, w_e, w_n = mass of water contained in a unit volume of material, and its evaporable and non-evaporable parts (Eqs. 4, 9-11);
 x = coordinate across the thickness of slab;
 α_0, α_1 = parameters in Eqs. (20) and (20a);
 $\beta = \beta_T \beta_H$ = relative hydration rate (Eq. 7);
 K = hygrothermic coefficient (Eq. 4);
 ρ, ρ_g = specific mass and specific weight of water;

Subscript sat . . . for saturation, $H = 1$;
 Primes in r', t', H' refer to non-dimensional variables Eq. (18).

INTRODUCTION

Recent materials research in concrete has shown that a correct prediction of the distribution and history of pore humidity in concrete structures is a problem of major importance. Its solution is inevitable for a realistic determination of shrinkage, creep, thermal dilatation and their effect on the stress state, deflections and crack formation. Furthermore, pore humidity directly affects strength, thermal conductivity and the rate of hydration or maturing. It plays a role in

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the problems of durability and fire resistance and is of particular interest for the assessment of radiation shielding characteristics or for answering the old question of uplift in dams. In addition, mathematical analysis of drying and wetting is indispensable for derivation of the stress-strain law from creep, shrinkage and thermal dilatation tests at variable humidity. It is also needed for interpretation of the sorption experiments in which achievement of hygral equilibrium is not guaranteed. Among engineering applications, the greatest need for prediction of humidity and water diffusion exists in the design of prestressed concrete pressure vessels for nuclear reactors and undersea concrete shells.

Although a large body of experimental data has been assembled over many years of research (for review cf. [21, 28-30, 39], e.g.), a reliable method of prediction is not presently available. The linear diffusion equation, which has been used extensively in the past [19, 39, 27, 21, 32, 23, 4, 5], is known to give a very poor fit of experimental data over long periods of time. Namely, as drying progresses the remaining moisture is lost with ever increasing difficulty and drying becomes much slower than an extrapolation of the initial drying curve which a linear diffusion theory would predict. This fact has been noted already by Carlson [11], Pickett [32] and others, and a conclusion was made [32] that diffusivity decreases with water content. This, however, makes the diffusion problem nonlinear and the classical analytical methods, such as the Fourier method [13], ineffective. Therefore Pickett [32] proposed to consider instead that diffusivity decreases with the time elapsed from exposure to drying environment, which preserves linearity of the problem and admits analytical solutions. Such an assumption is, however, only a crude approximation and does not allow a satisfactory fit of the data for various specimen thicknesses and shapes. It also violates the principle of objectivity of material, since a material property is made dependent on our choice of the instant of exposure to drying environment. Nevertheless, before electronic computers became available, no better formulation was possible.

Dependence of the diffusivity on pore water content was first considered by Pihlajavaara and co-workers [29, 26] who carried out numerical analyses of drying of slabs for various hypothetical forms of the above dependence. Although they did not report any attempts of fitting actual data, they observed that diffusivity probably decreases several times when passing from 100 % to 70 % relative humidity. Definite conclusions, however, have not been reached so far. This is partly due to the fact that until recently the known data on drying have been insufficient. They consisted mostly of weight measurements, while for a complete information measurements of moisture or pore humidity distributions throughout the specimen are necessary. These were made possible only when suitable probe-type humidity gages, especially the Monfore gage [2], were developed.

The intent of this paper is an analytical study of the dependence of diffusivity on pore humidity, temperature and other variables ⁽¹⁾. With this aim in mind,

⁽¹⁾ Some of the findings, notably those supporting Eq. (20), were presented at the ASCE Conference on Frontiers of Research and Practice in Plain Concrete, held in Allerton Park, University of Illinois, Urbana, in Sept. 1970, and have been briefly reported in Ref. [8a].

the mechanisms of diffusion will be also discussed, and the pertinent form of the diffusion equation will be derived from basic physical relationships.

DIFFUSION EQUATION FOR DRYING OF CONCRETE

The rate of diffusion of water may be characterized by the flux \vec{J} denoting the mass of water passing through a unit area perpendicular to \vec{J} per unit time. At uniform temperature, \vec{J} is a function of the gradient of the Gibbs' free energy μ per unit mass of evaporable water. This function must be linear for sufficiently small gradients. Thus

$$\vec{J} = -\tilde{c} \text{ grad } \mu \quad (1)$$

where \tilde{c} = coefficient characterizing the permeability of material, which is a function of temperature T and of the water content (concentration), w_e , of evaporable water per unit volume of porous material. Assuming water vapor as an ideal gas, the following well-known relation applies (cf. [6], e.g.):

$$\mu = (R/M) T \ln H + \mu_{sat}(T) \quad (2)$$

where R = gas constant, M = molecular weight of water, T = absolute temperature; $RT/M = 1360 \text{ atm.cm}^3/\text{g}$ (1405 kgf.cm/g) at temperature $T = 298 \text{ }^\circ\text{K}$ ($= 25 \text{ }^\circ\text{C}$) ($1 \text{ kgf} = \text{force kilogram} = 9.8066 \text{ N}$); H = pore humidity = $p_v/p_{sat}(T)$ where p_v = vapor pressure; $p_{sat}(T)$ and $\mu_{sat}(T) = p_v$ and μ at saturation. It should be noted that μ in each pore is the same for water vapor, capillary water and unhindered adsorbed water, since all of these phases may be considered to be in mutual thermodynamic equilibrium at any time.

For the sake of simplicity, only the case of quasi-uniform (although time-variable) temperature T will be considered (i.e., $\text{grad } T = 0$). This means that rapidly changing temperatures, as in fire exposure, are excluded. (Rapid changes of moisture content will also be left out of consideration because the latent heat of adsorption evolved or consumed would change temperature considerably.) Then, expressing μ in terms of T and H as mentioned, Eq. 1 may be rewritten as follows:

$$\vec{J} = -c \text{ grad } H \quad (3)$$

where

$$c = (R/M) T \tilde{c} / H \quad (3a)$$

Coefficient c , called permeability, depends on H and T . It probably also depends on $\text{grad } H$ if $\text{grad } H$ is large ⁽¹⁾.

⁽¹⁾ To be aware of all the simplifications implied, it should be noted that, in general, several kinds of diffusions, mutually coupled, could be involved even when the gradient of temperature is negligible. These could include flux of adsorbed water, capillary water and vapor, viewed as distinct separate processes, and the flux due to gradients of osmotic pressure which are produced as drying increases concentration of various ions dissolved in pore water. However, investigations described in the sequel show that an acceptable fit within the range of data presently available can be obtained without taking such effects into account.

Diffusion through concrete is so slow that various phases of water in each pore (vapor, capillary water and adsorbed water) remain almost in thermodynamic equilibrium at any time. Thus, the relationship between H and w at a constant T and a fixed degree of hydration is given by the well-known desorption or sorption isotherms [33, 30]. These may be written in a differential form [6, 8] as $dH = k dw$ where $k = (\partial H / \partial w)_T =$ function of $H =$ cotangent of the slope of the isotherm $w = w(H)$. When variable temperature T and the progress of hydration (aging, maturing) are taken into account, additional terms must be included [6, 8]:

$$dH = k dw + \kappa dT + dH_s \quad (4)$$

where $\kappa = (\partial H / \partial T)_w =$ hygrothermic coefficient [6, 8] = function of $H =$ change in H due to one degree change in T at constant w and a fixed degree of hydration; $dH_s =$ change (drop) in H caused by hydration during time interval dt at constant w and $T =$ self-dessiccation [37, 14]; $H_s(t) =$ pore humidity which would arise in time t in a sealed, initially wet specimen; w is understood as the total water content including both the evaporable water w_e and the combined (non-evaporable) water w_n per unit volume of material ($w = w_e + w_n$).

The rate of change of the mass w of water per unit volume of porous material is determined from the flux field by the relation

$$\partial w / \partial t = - \text{div } \vec{J} \quad (5)$$

expressing the condition of conservation of mass. Eliminating \vec{J} and w from Eqs. (1), (3), and (4), it follows:

$$\frac{\partial H}{\partial t} = k \text{div} (c \text{grad } H) + \frac{\partial H_s}{\partial t} + \kappa \frac{\partial T}{\partial t} \quad (6)$$

which represents the diffusion equation governing drying of concrete at variable, but almost uniform temperature.

Self-dessiccation H_s and coefficients k , c , and κ depend on the degree of hydration of cement paste. This may be conveniently characterized by the equivalent curing period t_e [6, 8], representing the period of curing at $H = 1$ and reference temperature T_0 for which the amount of water combined, w_n , would be the same as for a given history of H and T over a period t . Inasmuch as the progress of hydration is known to depend on T and H , t_e must be a function of H and T . The simplest possible relationship has the form:

$$dt_e = \beta_T \beta_H dt \quad (7)$$

where $\beta_T =$ function of T ; $\beta_H =$ function of H . The approximate dependence of β_H upon H , following from the observation [37] that hydration stops completely when $H \leq 0.8$, is shown in Figure 1; for numerical computations the expression $\beta_H \approx [1 + (7.5$

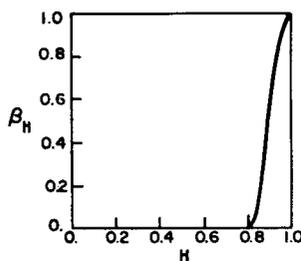


Fig. 1. — Dependence of relative hydration rates on humidity H .

— $7.5 H)^{-1}$] has been used [6, 8]. The influence of T upon the rate of hydration reaction is known to obey the Arrhenius equation for thermally activated processes. Thus

$$\beta_T = \exp \left(\frac{Q_h}{RT_0} - \frac{Q_h}{RT} \right) \quad (7a)$$

where $Q_h =$ activation energy for hydration; approximately $Q_h/R \approx 2500^\circ K$, as was determined [6, 8] from the data in Reference [15].

In a rigorous formulation, coefficients k , c , and self-dessiccation H_s must be considered as functions of t_e , and Eq. (7) as simultaneous with (6). It should be noted that the decrease in c as concrete matures is particularly strong (by orders of magnitude) in a young concrete. Also note that in the drying problem the values of t_e after exposure become non-uniform throughout the body, because β_H is less near the surface than in the core.

The slope of the desorption isotherm, characterized by k , is usually almost constant over a wide range of humidities such as $0.95 \geq H \geq 0.15$, especially for denser pastes [33]. Then, if the differences in k due to non-uniformity of t_e are negligible, Eq. (6) takes on the form:

$$\frac{\partial H}{\partial t} = \text{div} (C \text{grad } H) + \frac{\partial H_s}{\partial t} + \kappa \frac{\partial T}{\partial t} \quad (8)$$

where $C = kc =$ diffusivity (or diffusion coefficient) depending on H . This form of the diffusion equation is assumed in the numerical analyses presented in the sequel.

If T is constant, the rate of hydration is negligible (as in a mature concrete) and k is assumed as constant, Eq. (4) yields $H = k(w - w_0)$ where w_0 is a constant. Then Eq. (8) may be written as follows:

$$\partial w / \partial t = \text{div} (C \text{grad } w) \quad (9)$$

where C may now be regarded as a function of water content w .

Diffusion equation in terms of w has been preferred in most of the literature [19, 24, 23, 28-31, 4, 5]. This formulation is based on the Fick's law [9, 16] which expresses the mass flux as a function of the concentration gradient, that is

$$\vec{J} = -C \text{grad } w_e \quad (10)$$

where the presence of the evaporable water content w_e rather than w is to be noted ($w_e = w - w_n$). For the general case of variable T and progressing hydration, Eqs. (10) and (5) furnish

$$\frac{\partial w_e}{\partial t} = \text{div} (C \text{grad } w_e) - \frac{\partial w_n}{\partial t} \quad (11)$$

where the last term represents the rate of loss in the evaporable water content w_e due to hydration. This equation, usually with constant C , has been used in the past [5] to formulate drying in presence of hydration. It should be noted, however, that it involves certain error. Namely, the use of Fick's law, Eq. (10), is not justified when hydration proceeds because the distribution of pore volume available to evaporable water (porosity) becomes, along with t_e , non-uniform after the exposure to drying environment. Thus equal w_e values in various points do not correspond to equal values of H and μ , and Eqs. (1) and (10) are in contradiction.

The formulation of drying in terms of H rather than the water content thus seems preferable. There are also other reasons for it. The use of H appears to

be more practical when the solution of drying problem is intended to serve as the basis for rational analysis of creep and shrinkage effects [6, 7, 8]. Furthermore, for usual water-cement ratios, the drop in H due to self-dessiccation (as in sealed specimens) is known to be rather small [14] ($H_s \geq 0.97$, approximately) and can be neglected even if hydration has not yet terminated (as will be done in the numerical analyses in the sequel), while $\partial w_n / \partial t$ in Eq. (11) never has negligible values, unless hydration has ceased. Another reason is that the boundary conditions are usually expressed in terms of H.

Formulation of the problem in terms of vapor pressure p_v would clearly be completely equivalent to that in terms of H.

The rate of moisture exchange with the environment at the surface depends on the difference be-

$$\left. \begin{array}{l} \frac{\partial}{\partial x} \left(C \frac{\partial H}{\partial x} \right), \quad \frac{1}{r} \frac{\partial}{\partial r} \left(Cr \frac{\partial H}{\partial r} \right), \quad \frac{1}{r^2} \frac{\partial}{\partial r} \left(Cr^2 \frac{\partial H}{\partial r} \right) \quad \text{for } r > 0 \\ 2 C (\partial^2 H / \partial r^2), \quad 3 C (\partial^2 H / \partial r^2) \quad \text{for } r = 0 \end{array} \right\} \quad (13)$$

(slab) (cylinder) (sphere)

tween Gibbs' free energies per unit mass of water in concrete and in the environment, i.e., upon $\mu(H_{en}) - \mu(H)$ where H_{en} is the environmental humidity. Neglecting the effect of a difference between the surface and environmental temperatures (which is always present because of latent heats involved, but is small if the body dries slowly), the difference in μ is, according to (2), proportional to $\ln H_{en} - \ln H$. Thus, for small rates of transfer :

$$\vec{n} \cdot \vec{j} = -B (\ln H_{en} - \ln H)$$

where B = surface emissivity, which depends on T, circulation of air (and type of insulation, if any); \vec{n} = unit outward normal at the surface. Substituting for \vec{j} from (1), the boundary condition becomes (1) :

$$d \vec{n} \cdot \text{grad } H = \ln (H/H_{en}) \quad (12)$$

$$\text{where } d = c/B \quad (12a)$$

As special cases, one obtains the boundary conditions for a perfectly sealed surface, i.e., $B = 0$, $d \rightarrow \infty$ or $\vec{n} \cdot \text{grad } H = 0$, and for a perfect moisture transfer $B \rightarrow \infty$, $d = 0$, $H = H_{en}$. Note that d has the dimension of length and in the special case of a wall with a linear distribution of H (steady state) represents the thickness of concrete which is equivalent to the humidity jump at the surface. One can thus simply add thickness d to the specimen and consider the new surface as perfectly transmitting. In the general case, when H is not distributed linearly, this can be used as an approximate method. One should note, however, that d depends on H.

The equations presented above apply for both drying ($dH < 0$) and wetting ($dH > 0$). However, it must be remembered that because of partial irreversibility of the desorption isotherms, the value of k for sorption ($dH > 0$) is greater than for desorption ($dH < 0$). Since the variation of k with H is usually more pronounced for sorption, Eq. (8) is probably

(1) More accurately, considering the effect of the temperature difference between the surface and the environment, the right-hand side of Eq. (12) would read $\ln H_{en} - (T/T_{en}) \ln H$.

not applicable. In the analysis of experimental data which follows, the case of wetting will be left out of consideration.

The formulation presented above can be used for concrete or mortar, as well as pure cement paste, although with different values of the material parameters. This involves the assumption that the aggregate is either much less permeable than concrete or has about the same properties as cement paste. In a rigorous formulation the exchange of moisture between aggregate and cement paste would have to be considered as a separate local diffusion process coupled with Eq. (1) (1).

In the case of symmetrical drying of a slab or a rotationally symmetrical drying of an infinite slab, infinite cylinder and sphere, the expression for $\text{div}(C \text{ grad } H)$ takes on the one-dimensional forms :

where x denotes the thickness coordinate of a slab and r the radius coordinate of a cylinder or sphere.

NUMERICAL ANALYSIS OF THE NONLINEAR DIFFUSION PROBLEMS

The nonlinear diffusion problems may be solved by step-by-step integration in time which is best applied in conjunction with the finite difference method in the space coordinate x or r. The simplest of the step-by-step methods use forward differences, in which case the increments of H (or w) in each time step Δt can be computed from simple explicit formulas. This method, however, becomes numerically unstable, even for constant C, when $\Delta t > \Delta x^2 / (2 C)$, Δx being the step of grid across the specimen [38]. This would require an enormous number of time steps if the steady state is to be determined. Therefore, it is necessary to use in the time steps either backward or central differences, for both of which the numerical process at constant C is stable at any Δt and allows the time step to be increased as desired; when C depends on H, stability is not guaranteed, but still these methods are in this regard much more favorable. While the dampening of error in subsequent steps is stronger when backward differences are used, the central differences are usually more advantageous because of their greater accuracy. One of the variants of the latter method, called Crank-Nicolson method [38, 17], has been used in the present work.

As an example, let us consider an infinite cylinder and show equations of this method for the diffusion equation (8) with $dH_s = dT = 0$:

(1) It would be necessary to add to the right-hand side of Eq. (6) the term $-k \partial w_{ag} / \partial t$ where w_{ag} = water content of the aggregate per unit volume of concrete, w and H being now referred to the cement paste matrix alone. The local diffusion would be, at the simplest, expressed by a relation of the type $\partial w_{ag} / \partial t = a_1 w_{ag} + a_2 w$, where a_1 and a_2 are certain constants.

$$\left. \begin{aligned} & \frac{1}{\Delta r} \left(\frac{\bar{C}_{i+1/2}}{\Delta r} + \frac{\bar{C}_i}{2 r_i} \right) (H_{i+1, n+1} + H_{i+1, n}) \\ & + \frac{1}{\Delta r} \left(\frac{\bar{C}_{i-1/2}}{\Delta r} - \frac{\bar{C}_i}{2 r_i} \right) (H_{i-1, n+1} + H_{i-1, n}) - \left(\frac{2}{\Delta t} + \frac{\bar{C}_{i+1/2} + \bar{C}_{i-1/2}}{(\Delta r)^2} \right) H_{i, n+1} \\ & + \left(\frac{2}{\Delta t} - \frac{\bar{C}_{i+1/2} + \bar{C}_{i-1/2}}{(\Delta r)^2} \right) H_{i, n} = 0 \quad (\text{for } i = 2, 3, \dots, N) \end{aligned} \right\} \quad (14a)$$

$$\left. \begin{aligned} & \frac{\bar{C}_1}{(\Delta r)^2} (H_{2, n} + H_{0, n} + H_{2, n+1} + H_{0, n+1}) \\ & - \left(\frac{1}{\Delta t} + \frac{2\bar{C}_1}{(\Delta r)^2} \right) H_{1, n+1} + \left(\frac{1}{\Delta t} - \frac{2\bar{C}_1}{(\Delta r)^2} \right) H_{1, n} = 0 \quad (\text{for } i = 1) \end{aligned} \right\} \quad (14b)$$

where $\bar{C}_i = C [1/2 (H_{i, n} + H_{i, n+1})]$, $\bar{C}_{i+1/2} = C [1/4 (H_{i, n} + H_{i+1, n} + H_{i, n+1} + H_{i+1, n+1})]$; $\Delta r =$ constant step of the grid along the radius of cylinder; subscript n stands for the n -th time step $\Delta t = t_{n+1} - t_n$ and subscript i for the number of nodal point along the radius; point $i = N$ coincides with the surface and $i = 1$ lies on the axis of cylinder ($r_1 = 0$).

To formulate a general boundary condition at the surface (with $d \neq 0$), it is necessary to imagine an extension of the grid by a fictitious nodal point $i = N + 1$ located at distance Δr beyond the surface. Large oscillations about the correct solution can be avoided only if the boundary condition is imposed at the time t_{n+1} rather than $t_{n+1/2}$ [38], which yields,

$$\bar{H}(t) = \frac{1}{L} \int_0^L H(x, t) dx; \quad (\text{slab})$$

on substituting $\ln(H/H_{en}) \approx 1 - H/H_{en}$

$$d_{n+1/2} \frac{H_{N+1, n+1} - H_{N-1, n+1}}{2 \Delta r} = 1 - \frac{H_{N, n+1}}{H_{en, n+1}} \quad (15)$$

When the transfer of moisture is perfect ($d = 0$), this equation may be replaced by $H_{N, n+1} = H_{en, n+1}$. In the axis of cylinder ($i = 1$), the condition of symmetry, $H_{0, n+1} = H_{2, n+1}$, may be imposed. Equations for a slab and a sphere are analogous.

Equations (14) are in general nonlinear, since C depends on the unknown H -values at t_{n+1} . But if the changes in H over the step Δt are small, it is possible to substitute, at first, the values of C corresponding to $H_{i, n}$ which are known from the preceding step. Then Eqs. (14) for $i = 1, \dots, N$, along with the two boundary conditions, represent a system of $N + 2$ linear algebraic equations for the unknowns $H_{0, n+1}, H_{1, n+1}, \dots, H_{N+1, n+1}$. Having solved these values, the solution may be repeated for the C -values determined from $H_{i, n}$ and the values of $H_{i, n+1}$ just computed. Thus improved values of $H_{i, n+1}$ are obtained. Further improvements (iterations) are usually not advantageous since they are less efficient than decreasing the step Δt . Solution of a system of $N + 2$ linear equations is carried out in each time step Δt twice. Because the system has a tridiagonal band matrix, its solution is quite fast.

Experience showed that the numerical solution sometimes tends to exhibit spurious oscillations about the exact solution when C varies considerably within the time step. This is due mainly to the fact

that the nonlinear equations (14) are replaced by linear ones using the C -values corresponding to previous values of H . In all of the computations later described, this problem could be remedied by decreasing Δt .

For the evaluation of weight measurements it is necessary to compute the loss in weight of specimens, $\Delta W(t)$, from the time of exposure t_0 to any specified time t . Assuming, as before, that k is constant within the range of H considered, $\Delta W(t)/\Delta W(\infty) = (1 - \bar{H})/(1 - H_{en})$ (at a constant environmental humidity) where \bar{H} = average pore humidity, which is defined as follows :

$$\left. \begin{aligned} & \frac{2}{R^2} \int_0^R H(r, t) r dr; \quad (\text{cylinder}) \\ & \frac{3}{R^3} \int_0^R H(r, t) r^2 dr \quad (\text{sphere}) \end{aligned} \right\} \quad (16)$$

These integrals have been evaluated in the program by Simpson rule.

NONDIMENSIONAL VARIABLES

The number of material parameters involved in the drying problem may often be reduced by introduction of new variables. As an example, consider the typical problem of drying of an infinite cylinder, which is defined, according to Eqs. (8), (13), and (7) with uniform T , $dH_s = 0$ and $d = 0$, by the following equations for the function $H = H(r, t)$:

$$\left. \begin{aligned} & \frac{\partial H}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[C(H, T, t_e) r \frac{\partial H}{\partial r} \right] \text{ for } 0 < r \leq R, t > t_0 \\ & t_e = t_0 + \beta_T \int_{t_0}^t \beta_H [H(r, t)] dt \\ & H = 1 \text{ for } t = t_0, 0 \leq r \leq R \\ & H = H_{en} \text{ for } r = R, t > t_0 \\ & \partial H / \partial r = 0 \text{ for } r = 0, t \geq t_0 \end{aligned} \right\} \quad (17)$$

where R is the radius of cylinder. Introduce now the usual non-dimensional variables :

$$r' = \frac{r}{R}, \quad t' = (t - t_0) \frac{C_1}{R^2}, \quad H' = \frac{H - H_{en}}{1 - H_{en}} \quad (18)$$

where $C_1 = C (l, T, t_0)$. Then :

$\frac{\partial}{\partial r} = \frac{1}{R} \frac{\partial}{\partial r'}$, $\frac{\partial}{\partial t} = \frac{C_1}{R^2} \frac{\partial}{\partial t'}$, and Eqs. (16) are transformed into the following problem for the function $H'(r', t')$:

$$\left. \begin{aligned} \frac{\partial H'}{\partial t'} &= \frac{1}{r'} \frac{\partial}{\partial r'} \left(C' r' \frac{\partial H'}{\partial r'} \right) \text{ for } 0 < r' \leq 1, t' > 0 \\ t_e &= t_0 + \beta_T \int_{t_0}^{t'} \beta'_H dt' \\ H' &= 1 \text{ for } t' = 0, 0 \leq r' \leq 1 \\ H' &= 0 \text{ for } r' = 1, t' > 0 \\ \partial H' / \partial r' &= 0 \text{ for } r' = 0, t' \geq 0 \end{aligned} \right\} \quad (19)$$

where $C' = C (H, T, t_e) / C_1$, $\beta'_H = \beta_H (H)$
in which $H = H_{en} + (1 - H_{en}) H' (r', t')$.

For a sphere, substitution (18) is also applicable, and so it is for a slab, provided that R is replaced by the half thickness L .

Substitution (18) eliminates dependence of solution on the absolute value of C because only the ratio C/C_1 appears. Under certain conditions, which will be discussed later, dependence on specimen dimension R or L and on temperature T is also removed. Note, however, that the dependence upon environmental humidity H_{en} is not eliminated unless the problem is linear (i.e. $C = \text{constant}$).

FITTING OF DATA AND DEPENDENCE OF DIFFUSIVITY ON PORE HUMIDITY

On the basis of the experimental data obtained by conventional drying tests, in which an initially wet specimen ($H \equiv 1$) is exposed to a lower constant environmental humidity H_{en} , the material parameters for diffusion need be determined by sophisticated analyses. Such analyses can lead to definite results only if a sufficiently wide range of data has been collected for one and the same concrete, including various H_{en} , various dimensions of samples, various T , and sufficiently long time periods. The traditional measurements of the decrease in weight give relatively little information, since they can be fitted equally well with widely different material parameters, and measurements furnishing the distributions of H at various times are most desirable, as has already been pointed out. Thus, of the great amount of data on drying reported in the literature, only few data (mentioned in the sequel) have been found really useful for our purpose.

Inspecting formulation of the problem in terms of non-dimensional variables (Eq. 19), it is seen that the dependence on specimen dimension R or L is eliminated only if C is independent of grad H .

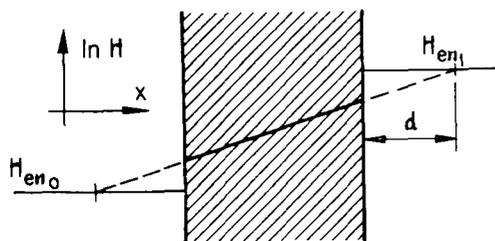


Fig. 2. — Geometrical significance of equivalent surface thickness.

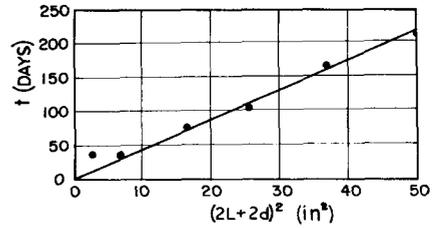


Fig. 3. — Time to reach 0.75 humidity at mid-slab for various slab thicknesses (Cf. Table 1), $d = 0.75$ mm.

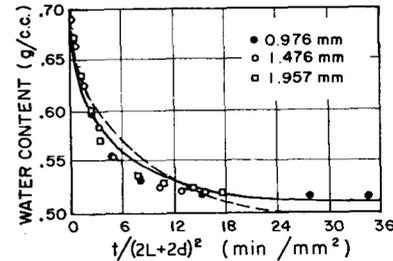


Fig. 4. — Water content of specimen versus non-dimensional time, assuming $d = 0.75$ mm (Cf. Table 1). Dashed line indicates linear theory.

Whether or not this is true can be determined, according to Eq. (18), from measurements on mature specimens of different thicknesses when the times needed to reach a certain H at a chosen point are plotted against L^2 or R^2 . If this plot can be fitted by a straight line, influence on grad H cannot be present. Data in Figure 3 show that this is indeed so, with the possible exception of very thin specimens in which grad H is high. But weight measurements shown in Figure 4 indicate that dependence on grad H is not needed even in the case of very thin slabs. (The value $d = 0.75$ mm in Figure 4, representing the equivalent surface thickness, Eq. 12a, was determined as a value for which the data for different thicknesses fall the closest to each other. The same value of d was assumed in Figure 3, although for the large thicknesses in this figure the value of d is unimportant and other values could yield an equally good fit.) In Ref. [26a] (Fig. 2), linear dependence on R^2 was also found.

Dependence of the diffusivity upon H was studied with the help of a computer program for drying, based on a method described previously. A number of shapes of the curve $C(H)/C_1$ with constant C_1

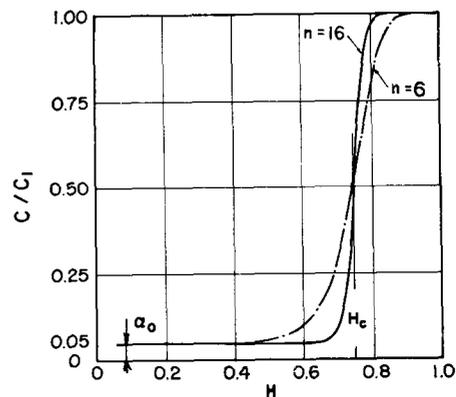


Fig. 5. — Diffusivity C versus H according to Eq. (20) for $n = 16$ and $n = 6$ ($\alpha_0 = 0.05$, $H_c = 0.75$).

TABLE I. — Material Parameters for the Data Analysed

| Figure | 3 | 4 | 6,7 | 8 | 9,10 | 11 | 12 |
|------------------------------------|------------------------------|--|--|--|---------------------|---|---|
| Reference | [1] | [22] | [3] | [2] | [20] | [24] | [4] |
| α_0 | — | 0.05 | 0.05 | 0.05 | 0.025 | 0.10 | 0.05 |
| h_c | — | 0.75 | 0.75 | 0.75 | .792 | 0.75 | 0.90 and 0.75 |
| n | — | 16 | 16 | 16 | 6 | 16 | 16 |
| C_1 (cm ² /day) | 0.349 | 0.144 | 0.382 | 0.187 | 0.239 | 1.93 | 0.269 |
| Type of specimen . | slabs | slabs | slabs | slabs | cylinders | spheres | equivalent to slabs |
| Thickness or diameter, 2L or 2R . | 1.5 to 7 in. | 1 to 2 mm | 6 in. | 12 in. | 6 in. | 4 in. | 28 cm |
| Environmental humidity | 0.3 to 0.4 & 0 to 0.05 | 0.47 | 0.10; 0.35; 0.50 | 0.10 | 0.50 | 0.0 | 0.0 |
| Age t_0 (days) | 7 | 25 °C | 7 | 7 | 7 | 30 | 2 and 5 |
| Test temperature .. | 70-75 °F | 25 °C | 73 ± 2 °F | 73 °F | 73 °F ± 2 °F | 75 °F | 25 °C |
| Water-cement ratio | 0.636 | | 0.60 | 0.45 | 0.657 | 0.50 | 0.82 |
| Mix proportions .. | 1 : 3.67 : 4.77 | | 1 : 2.83 : 5.26 | 1 : 2.61 : 1.75 | 1 : 3.26 : 3.69 | | |
| Remarks..... | Carbonate aggregate concrete | Cement paste in CO ₂ free air | Sand & gravel; 4.5 bags of cem. per cu. yard | Sand & gravel; 7 bags of cem. per cu. yard | Elgin sand & gravel | Thames irregular flint; cem : aggr. = 1 : 3 | Concrete; cube strength 156 kgf/cm ² |
| | | | | | | | Ferrocrete Cement |

have been selected and fed into the computer. The results of computations were output on the CALCOMP Plotter, in terms of non-dimensional variables (Eq. 18). These diagrams were then compared with the available data, which were also plotted in terms of non-dimensional variables, Eq. (18) (on the same scale). The curve $C(H)$ giving the relatively best fit over the whole range of data was sought by visual comparison.

First the relationships of the type $C = C_1 [\alpha_0 + (1 - \alpha_0) H^n]$ or $C_1 [1 - (1 - \alpha_0)(1 - H)^n]$ were considered. However, although a number of values were tried for constants α_0 and H_1 , no acceptable fit was obtained. (For the former of these relationships, graphs of solutions of drying of slabs for certain values of α_0 , H have already been presented by Pihlajavaara et al. [29, 26].) Therefore, curves with three parameters have been taken under considerations. Guided by some ideas on the diffusion mechanism, S-shaped curves of the type (shown in Figure 5) :

$$C(H) = C_1 \left(\alpha_0 + \frac{1 - \alpha_0}{1 + \left(\frac{1 - H}{1 - H_c} \right)^n} \right) \quad (20)$$

were tried. These finally allowed an acceptable fit of all of the known published data suitable for this purpose. The fits with $dt_e = dH_s = 0$ are demonstrated in Figures 6 to 11 and 4 by solid lines. The dashed lines represent the best possible fits by a linear theory with a constant diffusivity. It is seen that the nonlinear diffusion theory with diffusivity given by Eq. 20 is much better than the linear theory and its accuracy is acceptable for practical prediction of drying. It should be noted that the time plots in Figure 6 and the humidity distribution plots in Figure 7 were both fitted with one and the same expression for

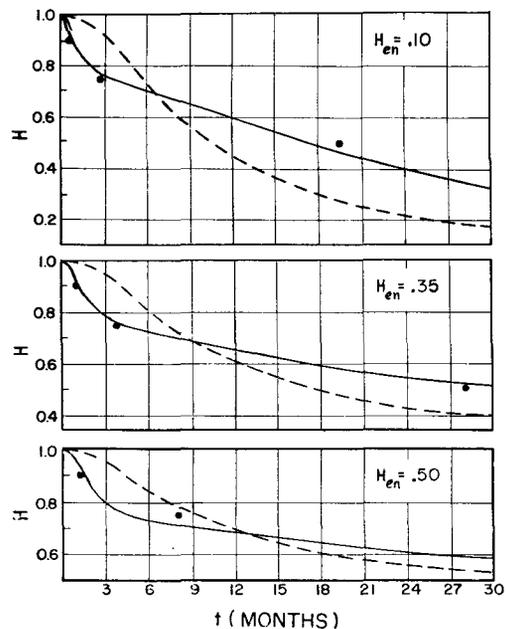


Fig. 6. — Mid-slab pore humidity versus time for data quoted in Table 1. Dashed lines represent linear theory.

$C(H)$, as they had to be. The same is true for Figures 8 and 9.

Especially noteworthy is the fact that, although the data in Figures 6-11, 4 included widely different concretes and pastes with thicknesses ranging from 1 mm to 7 inches and different absolute values of C , the values of the parameter H_c , characterizing the humidity at which C drops half-way between its maximum and minimum values were found to be

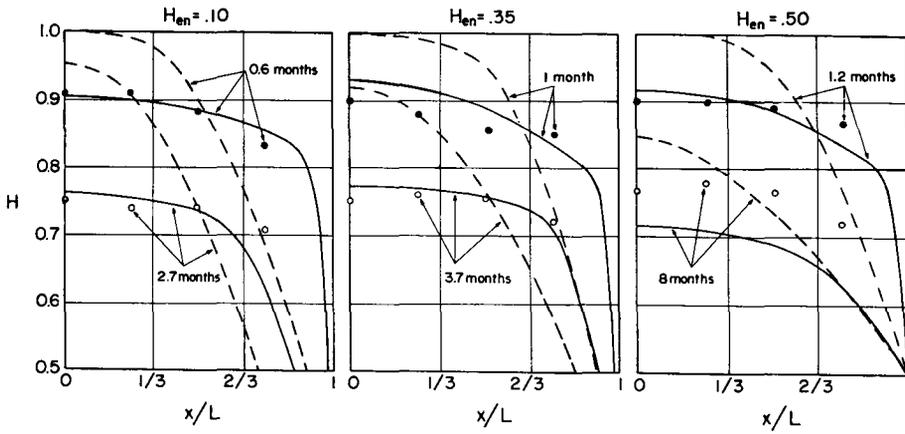


Fig. 7. — Distributions of H at various times for the same tests as in Fig. 6 (Cf. Table 1). Dashed lines represent linear theory.

the same; namely, $H_c = 0.75$ (Table I). Moreover, the values of parameter α_0 , representing the ratio $\min C/\max C$, were quite close even for different concretes and ranged between 0.025 to 0.10. The values of n , characterizing the spread of the drop in $C(H)$, were between $n = 6$ and $n = 16$. The typical variation of the diffusion coefficient with H_1 characterized by these values, is shown in Figure 5.

The absolute values of C_1 for different concretes vary more than H_c , and are larger for high water-cement ratios w/c [4, 5]. Analysis of the data of Aleksandrovskii [4] with $w/c = 0.82$ gives about 10-times higher value of C_1 . Moreover, these data seem to lead to different values of parameters α_0 and H_c in Eq. 20 (although for clear conclusions these data are insufficient and too scattered); this might be caused, however, by an error in conversion of w to H because for highly porous pastes, the value of k is not constant on desorption, having a smaller value near $H = 1$. Nevertheless, for dense pastes the value of C_1 seems to scatter much less than the crude linear theory, used for evaluation in the past, seemed to indicate [39]. They also scatter much less than permeabilities under hydraulic pressure [35]. The typical value is $C_1 \approx 0.25 \text{ cm}^2/\text{day}$.

The diagrams of the rate of weight loss plotted against the weight, which are identical with the

diagrams of $\partial \bar{H}/\partial t$ versus \bar{H} , shown in Figure 11, are often employed for determination of the diffusivity C [24, 19], making use of the fact that C should be proportional to the starting slope of the diagram. However, when C is variable, the straight portion of the diagram is very short and determination of the starting slope (which is proportional to $C(H_{en})$) just from data points is rather inaccurate, so that the whole diagram must be fitted as in Figure 11. Obviously, adjustment of the first half of the diagram to a straight line (as has often been performed) gives grossly distorted values of C .

It should be noted that expression 20 allows elimination of one parameter from the formulation of the problem. Namely, by expressing H in terms of H' (Eq. 18), Eq. (20) becomes :

$$C = C_1 \left(\alpha_0 + \frac{1 - \alpha_0}{1 + \alpha_1^n (1 - H')^n} \right) \quad (20 a)$$

where $\alpha_1 = \frac{1 - H_{en}}{1 - H_c}$

Thus, it is seen that both H_c and H_{en} disappear from Eqs. 19 and the solution depends only on the ratio α_1 (provided the initial humidity is 1.0).

SOME IMPLICATIONS FOR THE MECHANISM OF DIFFUSION

The dependence of diffusivity C upon H , as has just been found, has some interesting implications for the mechanism of diffusion. If the transfer of water were taking place mainly within the vapor phase, flux J would have to be about proportional to gradient of

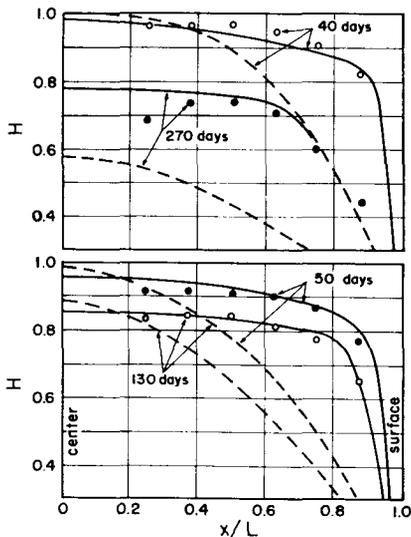


Fig. 8. — Distributions of H at various times for data quoted in Table 1. Dashed lines represent linear theory. (All are data from the same specimen).

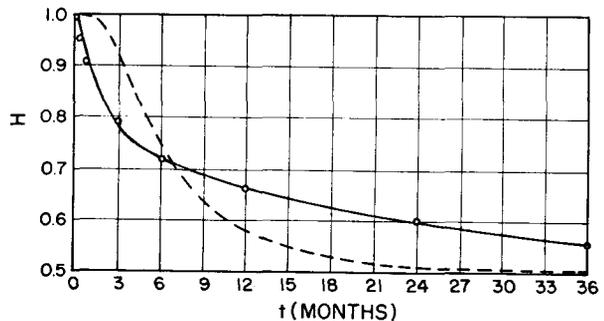
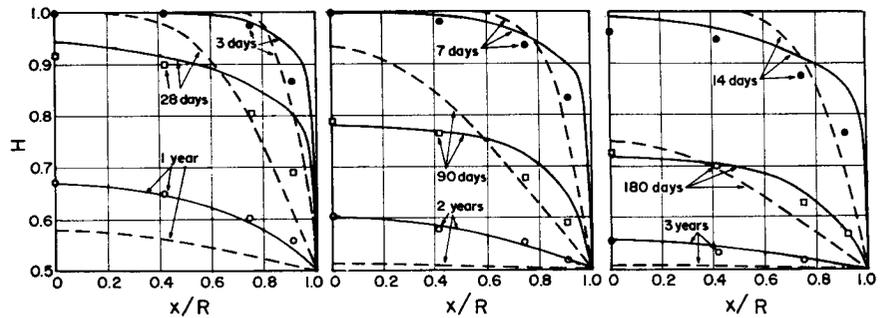


Fig. 9. — Mid-cylinder humidity H versus time for data quoted in Table 1. Dashed line represents linear theory.

Fig. 10. — Distributions of H at various times for data quoted in Table 1. (All are data from the same specimen).



vapor pressure p_v without regard to the value of H (at least for small J) and coefficient c in Eq. (3), as well as C, would have to be essentially independent of water content (or perhaps increase with decreasing water content because more space becomes available to vapor after drying). The substantial drop in C at drying can be explained only when flow of water within the thin adsorbed layers is considered to be the dominant mechanism at humidities below about $H = 0.6$. Above this limit, small capillary pores become filled and flow of capillary water, along with the upper (third to fifth) adsorbed layers, is of importance. Obviously, the adsorbed molecules are much less susceptible to flow than capillary water because they are held by strong surface forces. The variation of C thus corroborates the presently prevailing view of the diffusion mechanism which has been held so far for the reason that the mean free path of water molecules in vapor (about 800 \AA at 25°C) is many times greater than the size of continuous pores in concrete (whose average is about 15 \AA), so that the probability for a vaporized water molecule to pass through such a narrow pore is extremely small).

The fact that C is about constant for $H < 0.6$ is curious. The appearance of H in the denominator of Eq. (3a) indicates a tendency of an increase in the diffusivity as H drops down. But \bar{c} at the same time falls because forces holding adsorbed molecules at the surface increase as the thickness of multi-molecular adsorbed layers decreases with H. Constancy of C for $H < 0.6$ suggests that these two opposite tendencies just offset each other.

The analysis of data presented here does not allow conclusions about the diffusion coefficient at very low humidities, below about $H = 0.15$. It cannot be excluded that there is another drop in C when the adsorbed layers change from two molecule to one molecule thickness, which happens at about $H = 0.12$. Furthermore, it is possible that in very porous pastes

(or pastes with microcracks due, e.g., to previous shrinkage) C sharply rises when saturation ($H = 1$) is approached, since in a rather porous cement paste under pressure water fills larger voids, in which much of the water is out of reach of surface forces and is thus more susceptible to flow, while in a dense paste no space out of reach of surface forces is available to water.

INFLUENCE OF TEMPERATURE AND AGING

Regarding the effect of hydration (aging) upon drying, no sufficient series of data (for one and the same concrete) has been found in the literature. In the analysis of data in Figures 6 to 11 and 4, self-desiccation and change in C due to hydration after exposure to drying were considered as negligible, the latter assumption being reinforced by the fact that for $H \leq 0.8$ no hydration takes place [37]. Some idea on the effect of the length of curing prior to exposure can be obtained from the data in Reference [4] which indicate that the diffusivity C_1 for five days of moist curing is about 1.5 times smaller than for two days of moist curing. The dependence of C_1 upon t_e was well fitted in the form $C_1 = C_{10} (1 + 10/t_e)$ where C_{10} is a constant and t_e is in days. Extensive data on the aging effect were reported in Reference [39] (but analysis showed that the specimens could not have been in a stationary state whose existence was assumed).

The dependence of diffusivity C on temperature can be found by determining its values at various levels of temperature, in the same manner as before. Theoretically, assuming that a single mechanism is dominant in the diffusion process, the temperature effect should obey the rate process theory [9, 16, 18]

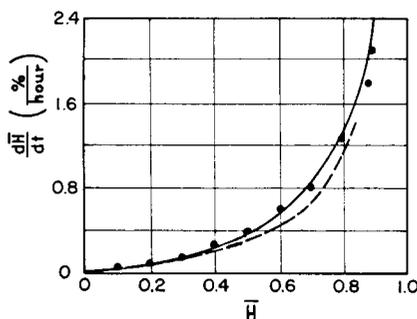


Fig. 11. — Rate of change of average humidity versus average humidity for a sphere. Data quoted in Table 1. (In fitting the initial slope of both curves was required to be the same).

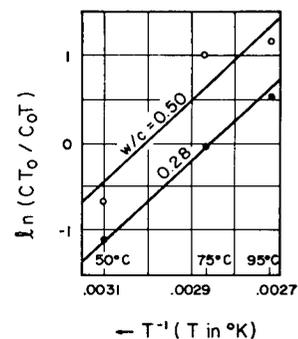


Fig. 12. — Dependence of diffusivity C on temperature for data quoted in Table 1.

which requires that the rate coefficient in Eq. (1) vary as follows :

$$\left(\frac{\tilde{c}}{\tilde{c}_0}\right)_{w, t_e} = \exp\left(\frac{Q}{RT_0} - \frac{Q}{RT}\right) \quad (21)$$

where T = absolute temperature, T_0 = chosen reference temperature; \tilde{c} and \tilde{c}_0 = the values of \tilde{c} at temperatures T and T_0 ; Q = activation energy (enthalpy) of the diffusion process. If the small change of slope of the desorption isotherm with T is neglected, i.e., k = constant, Eq. (21) yields (according to (2a) and the relation $C = kb$) :

$$\left(\frac{C}{C_0}\right)_{w, t_e} = \frac{T}{T_0} \exp\left(\frac{Q}{RT_0} - \frac{Q}{RT}\right) = f(T) \quad (21a)$$

For matching of experimental data, this equation may be rewritten as $\ln(CT_0/C_0T) = (Q/R) T^{-1} + \text{constant}$. The plot of $\ln(CT_0/C_0T)_{w, t_e}$ versus T^{-1} should thus be fitted with a straight line, whose slope then represents Q/R . This is shown in Figure 11 for various values of water-cement ratio. The value of the activation energy was found to be roughly equal to 9 300 cal/mole, although the amount of data points was certainly too small for any sweeping conclusion.

It should be noted that the numerous data from fire tests do not allow such a simple evaluation of Q because, in this type of test, temperature is not constant during the test as the specimen is dried. Also, the afore-mentioned diffusion equations do not apply for fire tests because they do not express coupled diffusions, i.e., the moisture flux due to grad T and the heat flux due to grad H . Nevertheless, it is at least possible to check simply whether the drying time at a rising temperature in fire test is greater than the drying time that would correspond to the terminal value of temperature using the above value of Q . This has been found true for fire test data from Reference [1], so that one can be at least satisfied that the value of Q found above is not contradicted.

According to the preceding discussion of the diffusion mechanism, the value of activation energy should increase as the adsorbed layers become thinner. The increase may be especially pronounced when the layers drop from two-molecules to one molecule in thickness, which happens at $H \approx 0.12$. However, this increase would not have much effect if the thinnest pores along each of the continuous passages through cement paste were only about two molecules in thickness, since in the thinnest pore, which has the dominant influence on the rate of flow, the adsorbed layer on each surface would remain one molecule thick for any $H > 0.12$. In such a case, Q would be essentially constant with H . The data on drying known at present do not allow us to answer these questions (1).

The dependence of C upon H or w at variable T and advancing hydration requires more careful examination. At variable T , coefficient C is not simply a function of H because the rate coefficient \tilde{c} in Eq. (1) depends, according to our view of the diffusion mechanism, essentially upon the distance from the solid surfaces or the thickness of the adsorbed layers. The latter is a function of w rather than H because at a change in temperature pore humidity varies (Eq. 4).

(1) Measurements of permeability of saturated concrete under hydraulic pressure [36] have shown that Q increases with porosity. This means that the distance from solid surface of the pores should indeed have an appreciable effect so that Q would grow as H decreases.

But in the case that the rate of hydration is not negligible, the water content is not a suitable independent variable either, as has been shown in the discussion after Eq. (11). According to Eq. (4) and the definition of hygrothermic coefficient K , C should be considered, at variable T , as a function of the so-called equivalent pore humidity H_{eq} defined by the relation [6, 8] :

$$dH_{eq} = dH - K dT \quad (22)$$

and representing the humidity at reference temperature T_0 for which the water content w is the same as for a given H and T , and the same t_e or degree of hydration. At variable T , H in Eq. (20) for C should be thus replaced by H_{eq} and Eq. (21a) yields :

$$C = [C(H_{eq})]_{T_0} f(T) \quad (22a)$$

In a numerical analysis at variable T , the increments of H_{eq} in each nodal point must be evaluated according to (22) for each time step Δt .

The hygrothermic coefficient K is always positive because w is known to decrease with T at constant H and t_e [40]. The approximate dependence of K upon H for about $H < 0.5$ may be derived [cf. 6, 8] from the theoretical B.E.T. equation [10, 33, 30] for free adsorption in multi-molecular layers. This equation reads :

$$w_a/w_1 = (1 - H)^{-1} - (1 - H + a_1 H e^{\Delta Q_{ad}/RT})^{-1} \quad (23)$$

where $a_1 \approx \text{constant} \approx 1$; w_a = mass of adsorbed water; w_1 = mass in a mono-molecular layer; ΔQ_{ad} = differential latent heat of absorption. Putting $w_e = w_a$ and differentiating this equation with respect to T at constant w_a , it follows, after rearrangements :

$$K = \frac{\Delta Q_{ad}}{RT^2} \frac{H(1 - H^2)}{1 + H^2(a_1 e^{\Delta Q_{ad}/RT} - 1)} \quad (24)$$

This expression confirms that $K > 0$ and satisfies the obvious limit condition $K \rightarrow 0$ for $H \rightarrow 0$. Furthermore, $K \rightarrow 0$ for $H \rightarrow 1$ because H cannot be raised above 1.0.

Measurements on sealed concrete specimens [25] furnished the value $K \approx 0.004$ per degree C at 35°C and $H = 0.87$. It was also found that K is higher for cooling than for wetting so that the diagram of H against T at constant w describes hysteresis loops. Other measurements on cement mortar, privately communicated by G. E. Monfore (Portland Cement Association, Skokie, Illinois) yielded the value $K \approx 0.005$ per degree C at 35°C and $H = 0.55$. A rough estimate of the plot of K versus T , based on these two data and theoretical considerations, is shown in Figure 13. (For calculations, expression $K \approx 0.0135 H(1 - H)/(1.25 - H)$ per degree C may be assumed.)

DIRECT MEASUREMENT OF PERMEABILITY

The simplest problem for analysis is the stationary permeation of moisture through a retaining wall subjected to different environmental humidities H_0 and H_1 at its two surfaces $x = 0$ and $x = 2L$ (fig. 14). In this case, the flux \vec{J} is constant in time as well as through the wall. Eq. (5) is automatically satisfied and only Eq. (1) or (3) need be used.

One direct method of determination of c may be based on measurement of the flux J and the pore humidity distribution $H(x)$ across the wall. Permea-

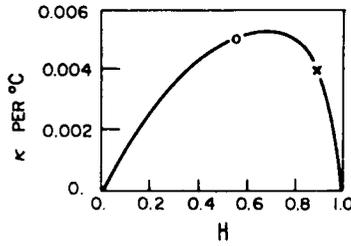


Fig. 13. — Approximate values of hygrothermic coefficient χ (Eq. 4).

bility c as a function of H may then be directly computed, according to (3), from the equation :

$$c(H) = -J (dH(x)/dx)^{-1} \quad (24 a)$$

This type of measurement has been carried out in the past [39, 27], but no interpretation regarding the variation of c with H or w has been attempted. (The evaluation has rather been made assuming a linear theory).

Another direct method can be based solely on measurement of flux J through a number of identical walls with the same H_0 but different values of H_1 . This gives J as a function of H_1 , $J = J(H_1)$. Then, integrating Eq. (3) one may write $\int_{H_0}^{H_1} c(H) dH = -L J(H_1)$, which by differentiation with respect to H_1 yields the formula :

$$c(H_1) = -L (dJ(H_1)/dH_1) \quad (25)$$

This method enables the measurement of pore humidity distribution to be dispensed with. Hence, one could use very thin specimens in which a stationary state of diffusion would arise very soon (in a few days for the thickness of 1 mm).

For a known $c(H)$ the stationary humidity distribution across a wall can be determined by solving

$$c_{sat} = \tilde{c}_1 \frac{\varrho_g}{\varrho^2} = \frac{C_1}{k_\varrho} \frac{M}{RT\varrho} \varrho_g = \frac{C_1}{k_\varrho} \frac{\text{cm}^2}{1,360 \text{ kp}} \frac{298^\circ \text{K}}{T} \frac{\text{kgf}}{1,000 \text{ cm}^3} \quad (27)$$

Eq. (5), i.e., the differential equation $dH/dx = J/c(H)$ for boundary values H_1, H_2 . The integral of this equation may be expressed by quadratures, but for any more complex formula for $c(H)$, such as Eq. (20), it is more convenient to use numerical step-by-step integration, e.g., the Runge-Kutta method (or a graphical integration, which is entirely sufficient for practical purposes). This has been done and Eq. (20) could thus be checked against the distribution of w reported by Wierig [39]. A satisfactory fit has been obtained, as is seen from Figure 14. The small misfit in Figure 14 could be caused, to some extent, by the fact that stationary diffusion possibly has not been reached, and also by the fact that Wierig's data, reported in terms of w , had to be approximately converted to H (assuming constant k).

TRANSITION INTO DIFFUSION IN SATURATED CONCRETE UNDER HYDRAULIC PRESSURE

Neglecting the effect of osmotic pressures, the seepage flow of water through saturated concrete

$$C_{sat} = \frac{c_{sat}\varrho}{\gamma\varrho_g w} = \frac{C_1}{\gamma k_\varrho} \frac{M}{RT\varrho} \frac{\varrho}{w} = \frac{C_1}{\gamma k_\varrho} \frac{\varrho}{w} \frac{298^\circ \text{K}}{T \times 1,360 \text{ atm}} \quad (28)$$

(1 atm = 1.033 kgf/cm² = 10.13 N/cm²).

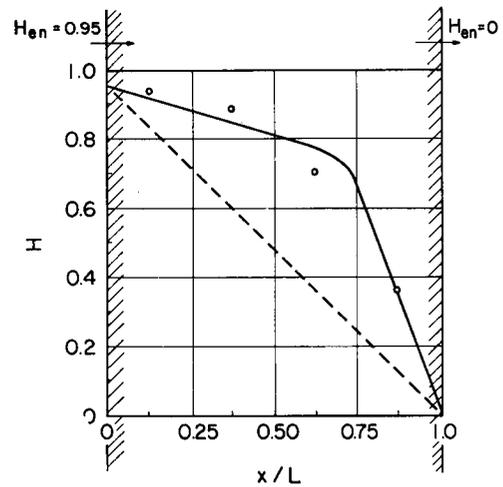


Fig. 14. — Theoretical stationary distribution of H compared with data quoted in Table 1. Dashed line represents linear theory.

under hydraulic pressure p in excess of one atmosphere is governed by Darcy's law :

$$J/\varrho = -c_{sat} \text{grad}(p/\varrho_g) \quad (26)$$

where $\varrho_g = 1 \text{ kgf}/1,000 \text{ cm}^3 =$ specific weight of water; $\varrho =$ specific mass of water; $p/\varrho_g =$ hydraulic head of pore water (dimension of length); $J/\varrho =$ volume of water flowing through a unit area in a unit time (dimension of $\text{cm}^3/\text{cm}^2 \text{ sec}$); $c_{sat} =$ permeability (dimension of cm/sec). It is known that c_{sat} (unlike c) is practically constant [35, 36] so that Eq. (26) is linear. Eq. (26) is a special case of Eq. (1) and follows by considering the relation $\mu = \varrho^{-1} p + \mu_{sat}(T)$ where $\varrho^{-1} = 1 \text{ cm}^3/\text{gram}$. Thus :

where $\tilde{c}_1 = \tilde{c}$ for $H = 1$. For usual cement pastes k_ϱ approximately equals 3 (for concretes, somewhat less).

Eq. (27) may be used to predict permeability of concrete under hydraulic pressure p if \tilde{c} in Eq. (1) changes continuously when passing from non-saturated to saturated concrete. The typical value which most data on drying showed was about $C_1 = 0.2 \text{ cm}^2/\text{day}$, which yields $c_{sat} \approx 0.5 \times 10^{-12} \text{ cm}/\text{sec}$. This equals about the lowest of the values recorded by Powers et al. [35] for very dense pastes. For more porous pastes, values up to 1,000 times greater have been observed. This indicates that in a very dense paste \tilde{c} is indeed continuous at $H = 1$, while in a more porous paste, it can exhibit a large jump upwards at $H = 1$.

The diffusivity C_{sat} for saturated concrete under hydraulic pressure may be derived from Darcy's law [26], continuity equation (5) and the relation $dw/w = \gamma dp$ where γ represents the effective volumetric compressibility of water in the saturated pores. These three relations yield the diffusion equation $\partial p/\partial t = C_{sat} \nabla^2 p$ in which the diffusion coefficient

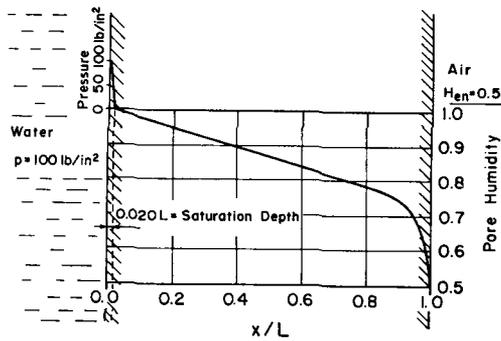


Fig. 15. — Theoretical stationary distribution of pore humidity in a retaining wall.

The proper value to be used for γ is questionable because an increase of p also compresses the solids. But it certainly must lie between $(25,000 \text{ kgf/cm}^2)^{-1}$, the volume compressibility of water alone, and about $(1.4 \times 10^6 \text{ kgf/cm}^2)^{-1}$, the volume compressibility of average concrete. According to the tests of Murata [27], the latter value gave acceptable agreement with some test results; then, for $k_0 \approx 2$ and $w/e = 0.3$ as typical values, $C_{sat} \approx 1,000 C_1$.

A very interesting problem is the depth of saturation by water in a retaining wall or submerged shell which is exposed at the surface $x = 0$ to water of pressure p_0 and at the surface $x = L$ to air of humidity $H_{en} = H_1$. To solve this problem, it is necessary to determine the relationship between grad p and grad H at the point where $H = 1$ and hydraulic pressure p (in excess of one atmosphere) is 0. Using the condition that J has the same value on both sides from this point, Equations (3), (26) and (27) furnish :

$$\frac{\partial p}{\partial x} = \left[\frac{\partial H}{\partial x} \right]_{H=1} \times 1,360 \text{ atm} \times \frac{T}{298 \text{ }^\circ\text{K}} \quad (29)$$

It is important to realize the magnitude of the coefficient in this equation; for instance, a 10 % drop in H over a certain length gives the same J (and the same grad μ) as 1,360 m drop in hydraulic head over the same length. To satisfy condition (29) automatically, the definition of H may be extended to pressures above saturation as follows :

$$H = 1 + p/(1,360 \text{ atm} \times T/298 \text{ }^\circ\text{K}) \text{ for } p > 0 \quad (30)$$

which can be verified by substitution in Eq. (29). The depth of penetration of water and the stationary pore humidity distribution can then be obtained by solving $H(x)$ solely from the nonlinear differential equation (3) (c being constant at $H \geq 1$) with the boundary conditions $H = H_1$ at $x = L$ and $H = H_0 =$ value of (30) for $p = p_0$ at $x = 0$. As an example, the values $H_1 = 0.5$ and $P_0 = 7.03 \text{ kgf/cm}^2$ ($= 70.3 \text{ m}$ of hydraulic head) have been chosen. Then $H_0 = 1 + 7.03/1,360 = 1.00518$, and using Eq. (20) with the typical parameters $\alpha = 0.05$, $H_c = 0.75$, $n = 16$ found above, the H -distribution shown in Figure 15 has been obtained. The stationary value of the depth of penetration of hydraulic pressure (point $H = 1$) has thus been found to be :

$$D_p = 0.020 L \quad (31)$$

which is astonishingly small ⁽¹⁾. The values of p_0 and H_1 chosen above are the same as in a test carried

⁽¹⁾ Lacking information on C as given here, somewhat different value of C was obtained by Bazant in a previous discussion of this problem [6]. Discussion of this effect in a non-analytical manner was given by Powers [34].

out by Carlson [12]. He measured (by Bourdon gages) hydraulic pressure in a 96-inch long pipe filled by concrete. The first gage was located 4 inches from the submerged surface and after the lapse of 7 years, none of the gages showed any pressure. Therefore, in this experiment $D_p < 0.04 L$, which well agrees with the above result. (However, in a rather porous concrete, in which \tilde{c} exhibits a jump upwards at $H = 1$ and c_{sat} is much higher than the value (27), a much deeper penetration D_p would be obtained. (Deep penetration also occurs when there are continuous cracks conducting water from the submerged surface.)

It should be realized that in the initial non-stationary state, the penetration of hydraulic pressure into a wall which was initially saturated (and without self-dessiccation) can be much deeper. As an example, consider that the humidity of the drying face is $H_1 = 0.9$ so that linear diffusion equation for drying applies. At the beginning, the depth of penetration of drying (defined, e.g., by the location of the point in which $H = 0.999$) is about the same as for an infinite halfspace, for which the depth of penetration is known to be [cf. 27] proportional to $\sqrt{C_1 t}$, where t = time elapsed from the exposure. Similarly, the depth of penetration of hydraulic pressure from the submerged face is proportional to $\sqrt{C_{sat} t}$. For $C_{sat} \approx 1,000 C_1$ (see discussion after Eq. 28), $\sqrt{C_{sat}} : \sqrt{C_1} \approx 32 : 1$. Thus, the front of drying and the front of hydraulic pressure would first meet only about $L/30$ from the drying face. (Later on, the transition point, i.e., point $H = 1$, $p = 0$ would recede toward the wet face as has already been discussed). The vast contrast between the initial location of the transition point and its terminal (stationary) location is a consequence of the fact that $C_{sat} \gg C_1$, which is, roughly speaking, due to the fact that in a saturated concrete very little water needs to flow into a pore to raise the hydraulic pressure substantially, while much more water must be removed to decrease H . This phenomenon initially offsets the opposite tendency stemming from the relation between gradients at the transition point, Eq. (29).

The above results are correct, however, only if there is no self-dessiccation whatsoever ($dH_s = 0$). Otherwise, the initial location of transition point will be much closer to the wet face (but still farther from it than the terminal location), which agrees with the experimental results [12].

The general problem of water diffusion at a constant T in a body in which there exists both non-saturated regions and saturated pressurized regions is formulated by Eq. (5) or (8) (with $dT = 0$), which applies to every point in the body provided that the definition of H is extended to the saturated regions according to Eq. (30), C is replaced by C_{sat} and dH_s is set at zero. The discontinuous jump between C and C_{sat} at the boundary between the two regions makes this problem highly nonlinear.

CHARTS FOR PREDICTION OF DRYING

In Figure 16, charts of the solutions to the drying problem given by Eq. (17) are presented. These charts, obtained by computer analyses, are plotted in terms of non-dimensional variables r' (or x'), H' and t' . The effect of hydration during drying is considered as negligible. For parameter α_1 , Eq.

SLAB

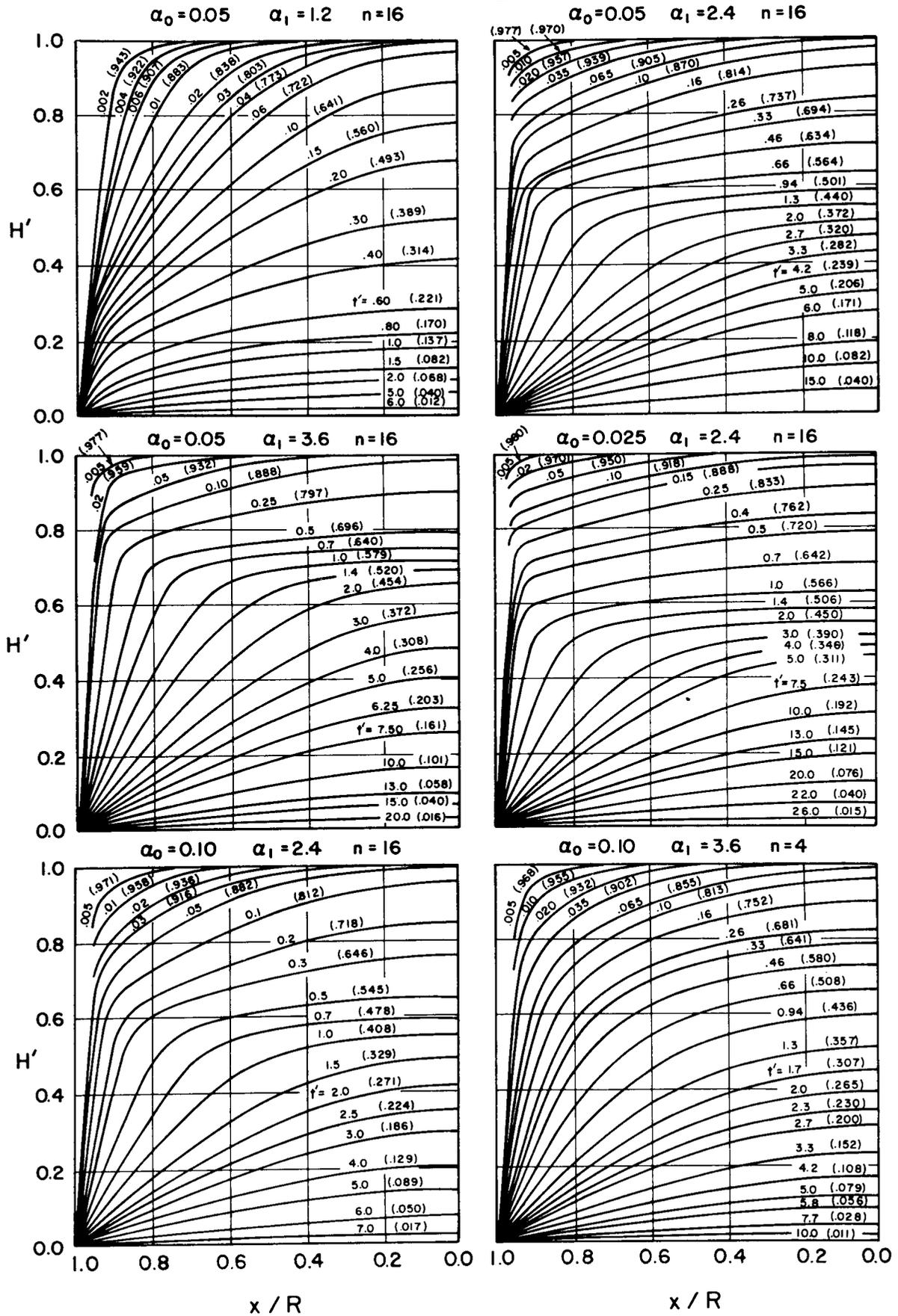


Fig. 16 (a)

CYLINDER

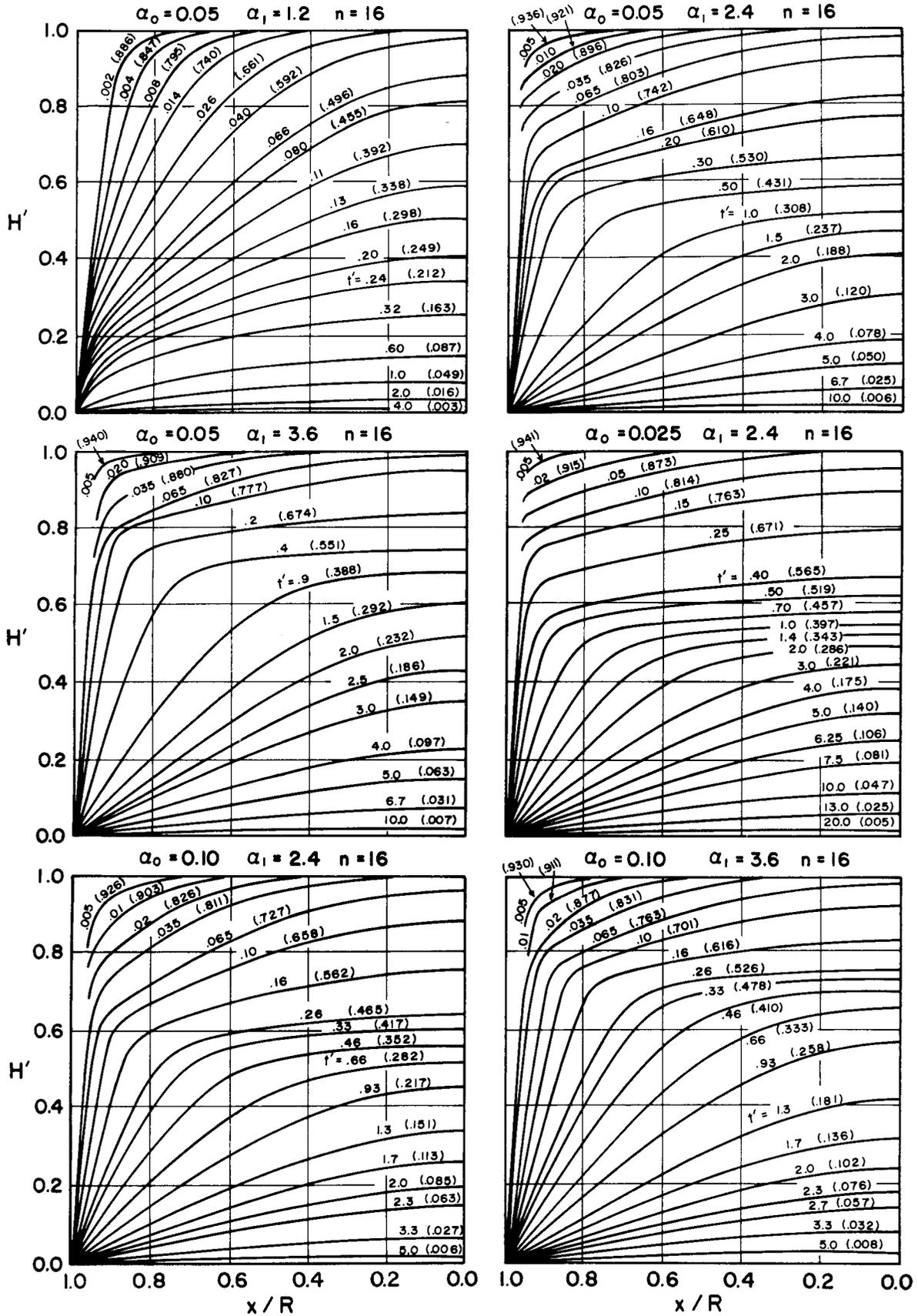
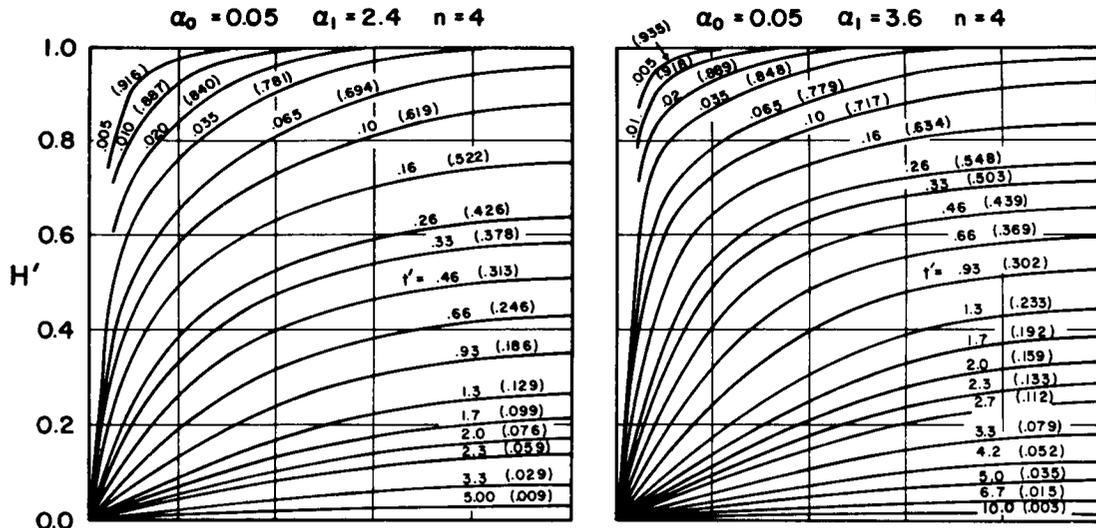


Fig. 16 (b)

CYLINDER



SPHERE

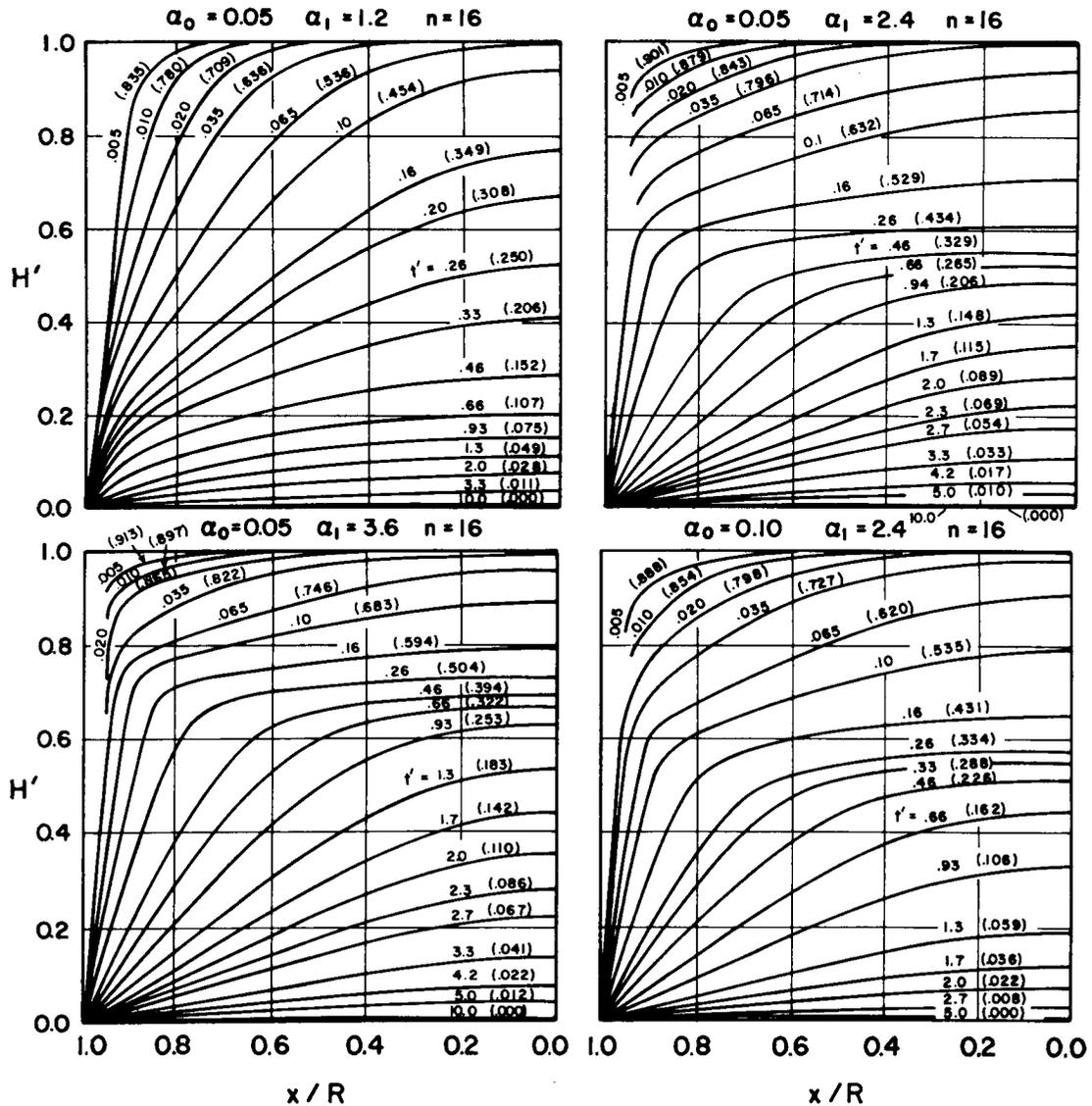


Fig. 16 (c)

Fig. 16. — Charts for drying of an infinite slab, infinite cylinder and sphere. Numbers in parentheses indicate the average humidity \bar{H} (Eq. 13) for each curve. (Similar diagrams for linear diffusion (or $\alpha_1 = 0$, of $\alpha_0 = 1$) can be found, e.g., in [13].)

(20a), various values were selected, allowing determination of the solution for any environmental humidity H_{en} by interpolation between the graphs. The parameter H_c in Eq. (20) may have any value. Two values of exponent n in Eq. (20), giving different steepness of the drop in C (Fig. 4), have been chosen. Note that the charts apply for any thickness, any value of C_1 , and any temperature. The graphs can be used for two purposes.

First, the charts allow C_1 to be determined from incomplete data, for instance when only the weight curve over a short time period is available. For this purpose, one has to assume the values of H_c , n , α_0 . One can also use the data for determination of both C_1 and H_c when a larger set of data is available.

Second, the charts enable the drying of concrete structures to be predicted. Even when the structural shape is not a slab, cylinder or sphere, it can be usually approximated by one of them. For instance, drying of the core of a prism can be assumed roughly equal to that of a cylinder with the same volume-to-surface ratio; drying of a cube like that of a sphere; or drying near the end of a prism like the average between the cases of a prism and a sphere, etc. If no data allowing determination of C_1 as above are available, one can roughly assume (for dense concretes) $C_1 = 0.25 \text{ cm}^2/\text{day}$, which is the average of the values from Table I.

It is useful to realize that nonlinear diffusion exhibits some very peculiar behavior. For example, as can be seen from the graphs in Figure 16, the core of a slab exposed to $H_{en} = 0.50$ would reach $H = 0.85$ within the time $t' = 0.43$, while for $H_{en} = 0$, the value $H = 0.85$ would be attained within the time $t' = 0.60$, i.e., after a longer period. This contrasts with the case of linear diffusion, in which the drying period for the latter case would be shorter. An intuitive explanation of this phenomenon is as follows: At a lower environmental humidity the surface region dries up quicker but this lowers its permeability and in effect hinders further loss of water from the core.

BASIC CONCLUSIONS

1. Diffusivity C strongly depends on pore humidity H , as is approximately expressed by empirical relation (20), in which, for dense concretes or cement pastes, $H_c \approx 0.75$, $\alpha_0 \approx 0.05$ to 0.10 , $n \approx 6$ to 16 , $C_1 = 0.1$ to $0.4 \text{ cm}^2/\text{day}$. The diffusion problem is thus strongly nonlinear.

2. The prediction of nonlinear diffusion theory, when compared with the data on drying, gives a much better correlation than does the linear diffusion theory. Drying of simple bodies can be determined from charts in Figure 16.

3. In the practically important range, C is independent of grad H . Despite nonlinearity of the problem, the rate of drying is inversely proportional to the square of dimensions of the body (Cf. Eq. 19).

4. Rate process theory gives acceptable results in relating the diffusivity C to temperature T (Eq. 21a).

5. The effect of aging is properly formulated by dependence of diffusivity C upon the equivalent hydration period t_e (Eq. 7).

6. The diffusion equation is more conveniently formulated in terms of pore humidity H rather than specific water content (concentration) w (Eqs. 6,8).

7. At variable temperature and advancing hydration, C should be taken as a function of equivalent pore humidity H_{eq} (Eq. 22) rather than H .

8. Because of nonlinearity of diffusion, the time needed for the core of a concrete body to dry to a certain pore humidity may be greater for a lower ambient humidity.

9. When temperature is raised at a constant water content, pore humidity H increases (Eq. 24). This effect is formulated by hygrothermic coefficient K (Eq. 4) whose dependence on H is roughly as shown in Figure 13.

10. A direct measurement of permeability is possible and may be best carried out according to Eq. (25).

11. Dependence of C upon H indicates that migration of water molecules along surface layers must be the dominant mechanism of diffusion.

12. In a wall exposed to pressurized water on one face and drying environment on the other face, the penetration of hydraulic pressure in a stationary state is a very small fraction of the thickness of wall (Fig. 15). This is a consequence of relation (29). In the initial nonstationary state, however, the penetration may be much deeper.

13. At a transition from a nonsaturated to a saturated state in dense concrete ($H = 1$), the diffusion coefficient increases discontinuously about 1,000 times. The rate of penetration of hydraulic pressure into saturated dense concrete is roughly 30-times higher than the rate of penetration of drying.

ACKNOWLEDGMENT

Most of the results presented in this paper have been obtained under National Science Foundation Grant GK-26030 on «Inelastic Deformations of Concrete due to Mass Transport». Grateful appreciation is due to Messrs. M.S. Abrams and G.E. Monfore, researchers at Portland Cement Association, Skokie, Illinois, for additional unpublished information on their test data.

RÉSUMÉ

Diffusion d'eau non linéaire dans le béton non saturé. — On présente les équations du séchage et de l'humidification du béton, étant supposé que le coefficient de diffusion et les autres paramètres du matériau sont déterminés par l'humidité interstitielle, la température et le degré d'hydratation. On examine le traitement numérique de l'équation de diffusion, et par comparaison des solutions calculées pour le séchage de dalles, cylindres et sphères, avec les nombreux résultats d'essais fournis par la littérature on démontre que le coefficient de diffusion diminue d'environ 20 fois lorsque l'humidité interstitielle passe de 0,9 à 0,6. On voit donc que le problème de la diffusion est nettement non linéaire. Ce résultat confirme aussi que la migration superficielle le long des couches constitue le mécanisme dominant de la diffusion. L'influence de la température se révèle en accord satisfaisant avec le concept d'énergie d'activation. L'effet de la température sur l'équilibre de l'humidité interstitielle est traduit par un coefficient

hygrothermique dont on donne les valeurs approximatives. On tient compte des variations des paramètres des matériaux avec l'âge du béton par l'intermédiaire d'une période équivalente d'hydratation dont l'accroissement dépend de la température et de l'humidité interstitielle. On montre que l'influence de l'humidité interstitielle sur la perméabilité peut être très simplement déterminée en mesurant le transfert permanent de l'eau à travers des parois minces dont l'une des faces est exposée à différentes conditions d'humidité ambiante. Afin de faciliter la prédiction du séchage de corps simples, on présente des diagrammes pour la résolution du problème du séchage non linéaire en fonction de variables non dimensionnelles. Enfin on examine la diffusion de l'eau dans des éléments présentant des régions de béton saturé sous une surpression hydraulique, à côté de régions de béton non saturé. On montre que de part et d'autre de la limite entre ces deux régions, le coefficient de diffusion varie d'environ 1 000 fois.

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