

DRYING OF CONCRETE AS A NONLINEAR DIFFUSION PROBLEM<sup>a</sup>

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ABSTRACT

Numerous experimental data on drying of concrete and cement paste are subjected to computer analysis. It is found that for a satisfactory fit of the data the diffusion coefficient must be considered to be a function of pore relative humidity (or specific water content), which makes the diffusion problem of drying nonlinear. The diffusion coefficient is shown to decrease sharply (about 20-times) when passing from 0.9 to 0.6 pore humidity, while below 0.6 it appears to be approximately constant. Improvement over the linear theory used in the past is very substantial and indicates that a realistic prediction of drying is possible.

RÉSUMÉ

Les dates expérimentales nombreuses sur le séchage du béton à l'air sont analysées à l'aide de l'ordinateur électronique. On trouve que pour un accord satisfaisant entre la théorie et résultats de mesure, le coefficient de diffusion doit être considéré comme une fonction de l'humidité relative dans les pores (ou le content spécifique de l'eau). Cette dépendance transforme le problème de diffusion à un problème non-linéaire. On montre que le coefficient de diffusion  $C$  décroît fortement (à peu près 20-fois) en passant de l'humidité 0.9 à 0.6 dans les pores, tandis qu' au-dessous de 0.6 il apparaît comme constant. L'amélioration à l'égard de le théorie linéaire utilisée dans le passé est très substantielle et indique qu' une prédiction réaliste du séchage est possible.

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Prediction of the distribution and time dependence of water content in concrete structures is a problem of considerable practical importance. It is needed for the determination of shrinkage, creep, thermal dilatation, strength, durability, rate of hydration, thermal conductivity, fire resistance and radiation shielding, and is especially important in the design of prestressed concrete pressure vessels for nuclear reactors. However, a satisfactory method of prediction is not available at present. The linear diffusion theory, which has been used in the past, is known to give a very poor correlation with test data. In particular, it is observed that with the progress of drying the remaining moisture is being lost with ever increasing difficulty and much slower than a linear diffusion theory would predict. This fact has been noted already by Carlson (7) and Pickett (15). The latter proposed to account for it assuming the diffusion coefficient  $C$  to decrease with the period of drying. Although with the data and computing devices available at that time no better formulation was possible, it should be pointed out that such an assumption is not generally acceptable since it makes a material property dependent on our choice of the instant of exposure and does not allow a satisfactory fit of the data for various thicknesses analyzed below.

Therefore, the apparent decrease of the diffusion coefficient  $C$  with the period of drying must be associated with some other variable. It is postulated here that this variable is the specific water content of concrete,  $w$ , or the pore humidity  $H$  (relative vapor pressure). The dependence of  $C$  upon  $H$  has in fact been anticipated since the earliest investigations. But solutions of the drying problems could not have been obtained before electronic computers became available because the above dependence makes the diffusion problem non-linear, and the usual solution by Fourier method inapplicable. Numerical computer analyses of drying of slabs for certain forms of the dependence  $C = C(w)$ , such as  $C = C_0 + C_2 w^n$  where  $C_0$ ,  $C_2$  and  $n$  are constants, have been studied by Pihlajavaara and co-workers (12,13,14) who concluded that the diffusion coefficient  $C$  decreases several times when passing from  $H = 1.0$  to  $H = 0.7$ . But no definite conclusions have been made and no attempts of fitting the data on drying and determining the dependence of  $C$  upon  $w$  or  $H$  have been reported. It should be noted, however, that until recently the data available have been insufficient for this purpose. Namely, an unambiguous determination of the dependence of  $C$  upon  $H$ , which is the primary purpose of this paper, requires the conventional weight measurements during drying to be complemented by direct measurements of the distribution

of  $w$  or  $H$  within the specimen, which could be conveniently carried out only after the development of suitable probe-type humidity gages, especially the Monfore gage (2).

#### Mathematical Formulation of Drying of Concrete

According to the Fick's law, the specific water content of cement paste or concrete,  $w$  (mass per unit volume), should satisfy the following partial differential equation:

$$\frac{\partial w}{\partial t} = \text{div}(C \text{ grad } w) \quad (1)$$

where  $t$  = time and  $C$  = diffusion coefficient = function of  $w$ . This equation applies only when the change of material properties due to hydration is negligible (as in old concrete or low  $H$ ), the degree of hydration is uniform throughout the body and temperature  $T$  is constant. Alternatively, drying of concrete can be also described in terms of pore humidity  $H$  since, at constant  $T$  and a fixed degree of hydration,  $dH = k dw$  where  $k$  = function of  $H$  = co-tangent of the slope of the desorption isotherm  $w = w(H)$ . Thus  $\partial w / \partial t = k^{-1} \partial H / \partial t$  and  $\text{grad } w = k^{-1} \text{grad } H$ , so that Eq. (1) yields

$$\frac{\partial H}{\partial t} = k \text{ div}(c \text{ grad } H) \quad (2)$$

where  $c = C/k$ , which can be shown to represent permeability and equal the mass flux due to a unit gradient of  $H$ . For dense cement pastes and concretes,  $k$  is usually almost constant from  $H = 0.95$  down to about  $H = 0.2$  (16). Then Eq. (2) simplifies as follows

$$\frac{\partial H}{\partial t} = \text{div}(C \text{ grad } H) \quad (3)$$

where the diffusion coefficient  $C$  is the same as in Eq. (1), except that it must be regarded as a function of  $H$  rather than  $w$ .

Equations (1) and (2) or (3) are obviously equivalent. It should be noted, however, that the formulations in terms of  $w$  or  $H$  would not be equivalent if the change of material properties due to hydration were considered (as is necessary for young concrete) or the temperature were not constant. In this case Eq. (2) must be expanded by additional terms (6) expressing self-desiccation due to hydration and temperature effect upon  $H$ . Pore humidity is the more suitable variable since  $H$  (unlike  $w$ ) is directly related to the Gibbs' free energy per unit mass of evaporable water,  $\mu$ , whose gradient is the actual driving force of diffusion. It should be noted that this gradient is not proportional to the gradient of concentration or  $\text{grad } w$ , since the degree of hydration, and thus also the pore volume available to



computer analyses reported in the sequel. In this method, the analysis of each time step is carried out twice, first with the C-values corresponding to the initial values of H in the time step considered, and subsequently with the improved C-values corresponding to the average value of H within the time step determined from the first analysis.

For the evaluation of weight measurements it is necessary to compute the loss in weight of specimen,  $\Delta W(t)$ , from time  $t_0$  to time  $t$ . Assuming  $k$  to be a constant,  $1 - \Delta W(t)/\Delta W(\infty) = (\bar{H}(t) - H_{en}) / (1 - H_{en})$  where  $\bar{H}$  = average of H,

$$\bar{H}(t) = \frac{1}{L} \int_0^L H(x,t) dx, \quad \frac{2}{R^2} \int_0^R H(r,t) r dr, \quad \frac{3}{R^3} \int_0^R H(r,t) r^2 dr \quad (6)$$

(slab)                                      (cylinder)                                      (sphere)

Data Fitting and Variation of the Diffusion Coefficient with Humidity

For fitting of experimental data it is expedient to reduce the number of variables in the problem as much as possible. For a cylinder or sphere, this may be achieved by introducing, instead of  $t, r, H$ , new non-dimensional variables  $t', r', H'$  defined as follows

$$r' = \frac{r}{R}, \quad t' = \frac{C_1}{R^2} (t - t_0), \quad H' = \frac{H - H_{en}}{1 - H_{en}} \quad (7)$$

where  $C_1$  = value of  $C$  at  $H=1$ . For a slab,  $L, x$  and  $x'$  appears in place of  $R, r$  and  $r'$ . Noting that  $\partial/\partial r = R^{-1} \partial/\partial r'$ ,  $\partial/\partial t = C_1 R^{-2} \partial/\partial t'$ , Eqs. (4) and (5) for a cylinder, e.g., become:

$$\left. \begin{aligned} \frac{\partial H'}{\partial t'} &= \frac{1}{r'} \frac{\partial}{\partial r'} \left( \frac{C(H)}{C_1} r' \frac{\partial H'}{\partial r'} \right) \text{ for } 0 < r' \leq 1, \\ \frac{\partial H'}{\partial t'} &= 2 \frac{C(H)}{C_1} \frac{\partial^2 H'}{\partial r'^2} \text{ for } r' = 0 \quad (t' > 0) \\ H' &= 1 \quad \text{for } t' = 0 \text{ and } 0 \leq r' \leq 1 \\ H' &= 0 \quad \text{for } t' > 0 \text{ and } r' = 1 \\ \partial H' / \partial r' &= 0 \quad \text{for } t' \geq 0 \text{ and } r' = 0 \end{aligned} \right\} \quad (8)$$

The solution  $H(t', r')$ , as well as  $H(t', x')$ , is thus seen to become independent of  $R$  or  $L$ , even if  $C$  depends upon  $H$ . The dependence upon  $C$  is by variables (7) reduced to a dependence upon the ratio  $C(H)/C_1$ . But owing to the presence of  $H$ , which equals  $H_{en} + (1 - H_{en})H'$ , in the first of Eqs. (8), the dependence upon  $H_{en}$  cannot be eliminated, except for special forms of the function  $C(H)$ , such as Eq. (8) introduced in the sequel (or when the problem is linear).

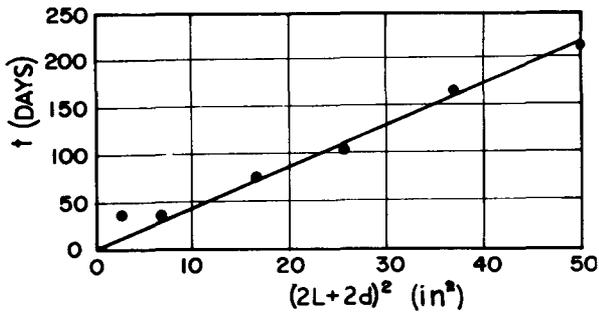


FIG. 1

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

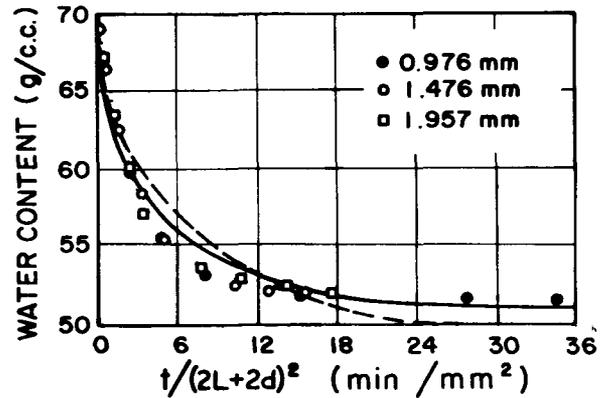


FIG. 2

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

According to the non-dimensional variables (7) just discussed, the times needed to reach a certain  $H$  in the centers of specimens of different thicknesses ought to be proportional to  $L^2$  or  $R^2$ , in spite of the nonlinearity of the problem. Data in Fig. 1 confirm it, with the possible exception of very thin specimens in which grad  $H$  is high. But the weight measurements in Fig. 2 are seen to be in approximate coincidence when plotted in the nondimensional time  $t'$ , Eq. (7), provided that approximately the thickness  $d = 0.75$  mm be added to the specimens to account for the finite rate of moisture exchange at the surface which is not much larger than the drying rate of very thin specimens. For the sake of uniformity, the value of  $d = 0.75$  mm was assumed even for the data in Fig. 1, although for the large specimen thicknesses in this figure other values of  $d$  (e.g.  $d = 0$ ) would allow an equally good fit. It should be noted that the fits as in Figs. 1 and 2 would be impossible if  $C$  depended on grad  $H$ .

Variation of the diffusion coefficient  $C$  with  $H$  has been investigated with the help of a computer program for drying of slabs, cylinders and spheres, based on the method outlined above. A large number of shapes of the curve  $C(H)$  have been selected and the results of computations have been output on the CALCOMP Plotter, in terms of the non-dimensional variables (7). Comparing visually these diagrams with the available test data, plotted in the same variables, the curve  $C(H)$  giving the relatively best fit over the whole range of data for one and the same concrete has been sought. Linear combinations of linear functions and power functions of various degrees in

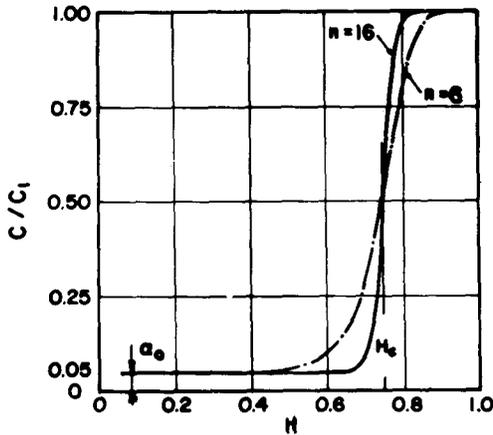


FIG. 3

Diffusion coefficient  $C$  versus  $H$  according to Eq. 9 for  $n = 16$  and  $n = 6$  ( $\alpha_0 = 0.05$ ,  $H_c = 0.75$ ).

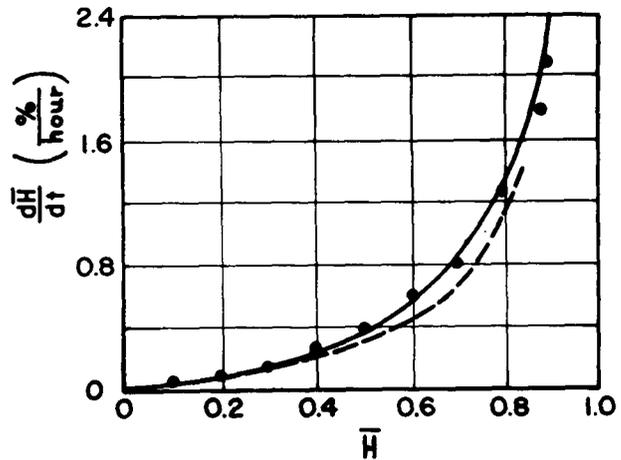


FIG. 4

Rate of change of average humidity versus average humidity (Cf. Table 1). (Dashed line represents linear theory. The initial slopes were assumed as identical.)

$H$  and  $(1 - H)$  did not allow an acceptable fit. But an S-shaped curve of the type (shown in Fig. 3):

$$C(H) = C_1 \left( \alpha_0 + \frac{1 - \alpha_0}{1 + \left( \frac{1 - H}{1 - H_c} \right)^n} \right) \tag{9}$$

was found to be satisfactory, as is demonstrated by the solid line fits in Figs. 4 to 9. For comparison, the best possible fits based on a linear theory (i.e. with constant  $C$ ) are shown by the dashed lines. The nonlinear theory is obviously far superior. It should be noted that the time plots in Fig. 5 and the distribution plots in Fig. 6 were all fitted with one and the same expression for  $C(H)$ , as they had to be. The same can be said about Figs. 7 and 8. Noteworthy is also the fact that the values of parameter  $H_c$ , characterizing the location of the drop in the curve  $C(H)$ , were found to be about the same for different concretes or cement pastes, notably about  $H_c = 0.75$  (see Table 1). Furthermore, the values of parameter  $\alpha_0$ , representing the ratio  $\min C/\max C$ , were also quite close and equal about 0.05 (Table 1). The values of the exponent  $n$ , characterizing the spread of the drop in  $C(H)$  were between  $n = 6$  and  $n = 16$ . The absolute values of the diffusion coefficient, characterized by the parameter  $C_1$ , were found to scatter more than the other parameters (Table 1), especially in dependence on the  $w/c$  (water-cement) ratio, as is documented, e.g., by the data of Aleksandrovskii (4,5) for  $w/c = 0.82$  which yield about 10-times higher value of  $C_1$  than most data

in Table 1. (For a study of the dependence of C upon H these data were found to be insufficient.)

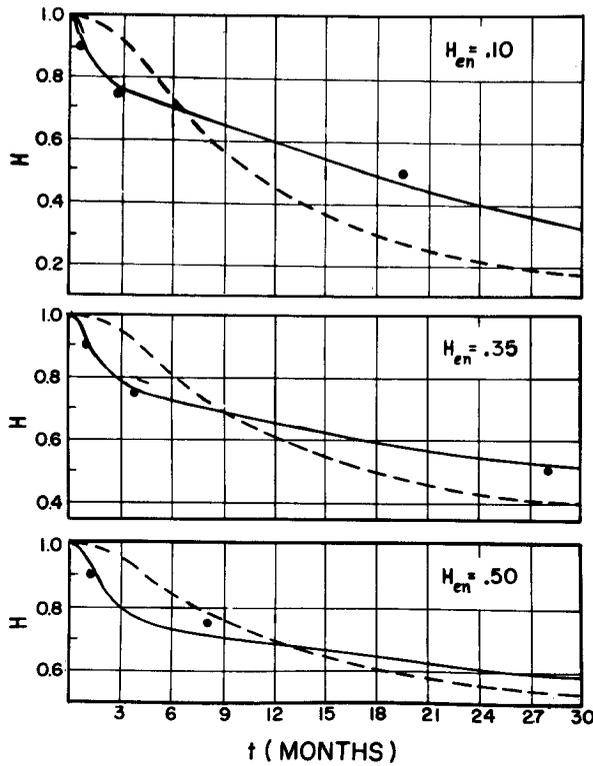


FIG. 5  
Mid-slab humidity  
(Cf. Table 1).  
Dashed lines represent  
linear theory.

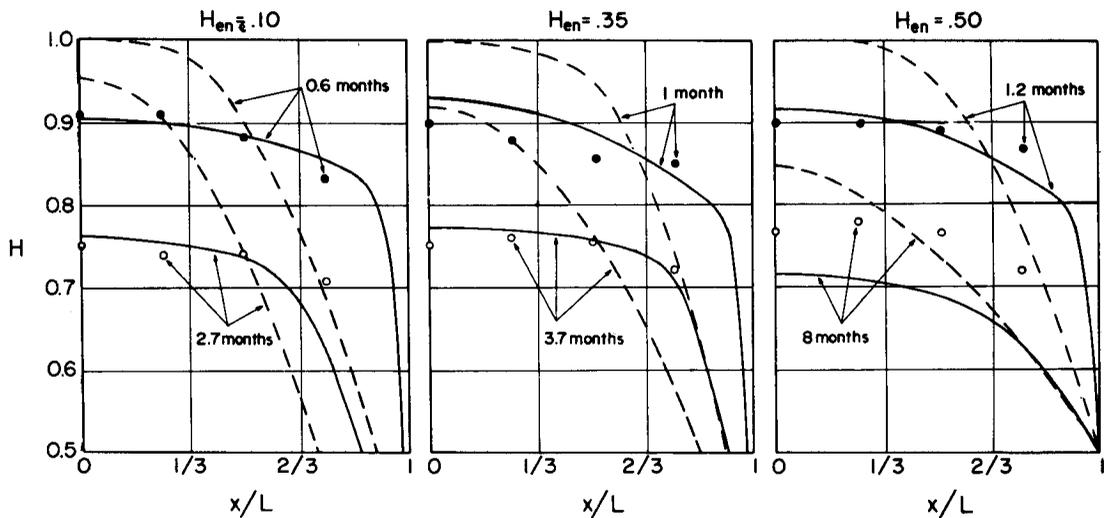


FIG. 6

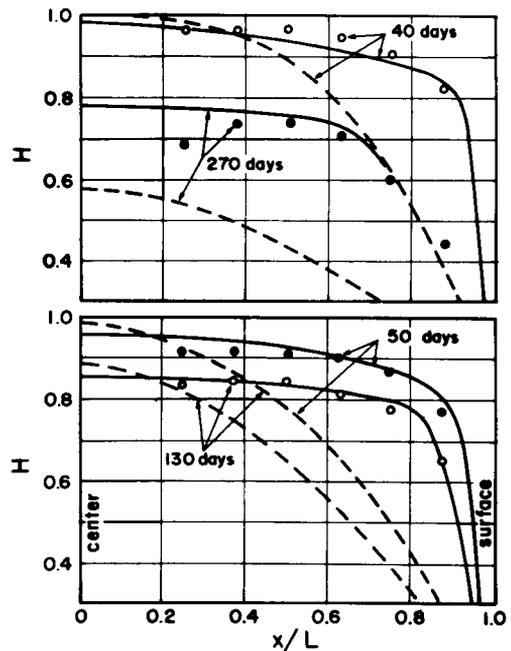
Distributions of H at various times for the same tests as in Fig.5  
(Cf. Table 1). Dashed lines represent linear theory.

TABLE 1  
Material Parameters for the Data Analyzed

Figure Reference	1 (1)	2 (10)	5,6 (3)	7 (2)	8,9 (9)	4 (11)	(4)
$\alpha_0$	-	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 <sup>2</sup> /day)	.349	.144	0.382	0.187	.239	1.93	.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		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 <sub>2</sub> 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 kp/cm <sup>2</sup>

FIG. 7

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



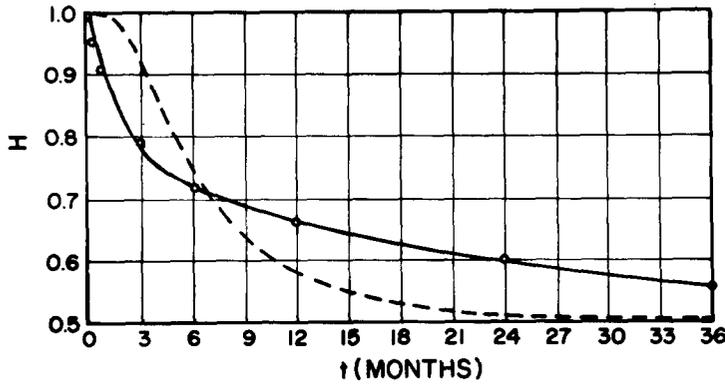


FIG. 8  
Mid-cylinder humidity H versus time for data quoted in Table 1. Dashed line represents linear theory.

Expression (9) has the advantage of allowing one further parameter to be eliminated from the problem given by Eqs. (4) and (5). Namely, by expressing H in terms of H' as given by Eq. (7), expression (9) takes the form:

$$C = C_1 \left( \alpha_0 + \frac{1 - \alpha_0}{1 + \alpha_1^n (1 - H')^n} \right) \quad \text{where} \quad \alpha_1 = \frac{1 - H_{en}}{1 - H_c} \quad (10)$$

According to Eqs. (8), the solution is thus found to depend only upon the ratio  $\alpha_1$  rather than on both  $H_c$  and  $H_{en}$  individually.

The shape of the curve C(H) is of interest for the mechanism of water diffusion through cement paste and concrete. If the flow of vapor were the dominant mechanism in water transport, the diffusion coefficient C would have to be essentially independent of water content or, perhaps, increase with decreasing H because more space becomes available to vapor after drying. The substantial drop in C at drying can be explained only when flow of water

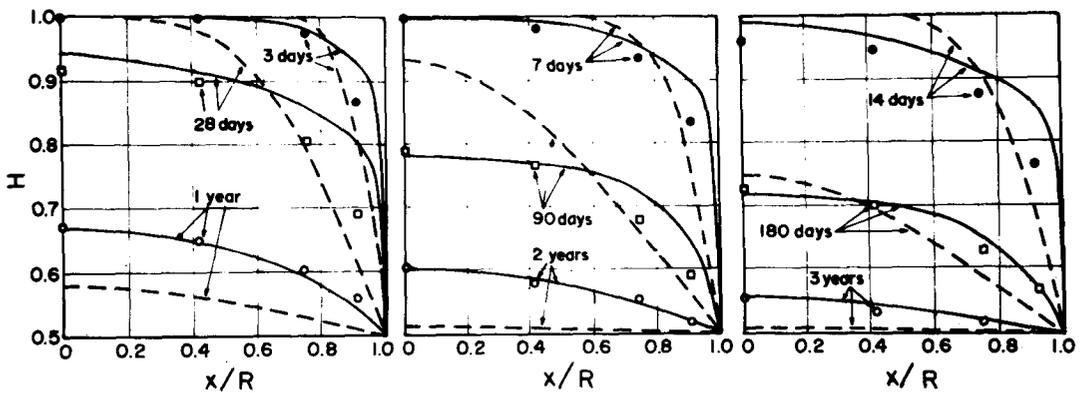


FIG. 9

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

molecules along thin adsorbed layers within the reach of solid surface forces is considered to be the prevailing mechanism at low humidities, such as  $H < 0.6$ , while above this limit the flow of capillary water (which comprises water whose distance from the pore surface is more than about five molecules) is of importance. The drop in  $C$  is probably due to a transition from a flow of capillary water (with a flow along the upper adsorbed layers) into a flow of firmly held molecules along adsorbed layers of two or three molecules in thickness. Our conclusions thus corroborate the presently prevailing view of the diffusion mechanism, which has been originally introduced for other reasons.

It is curious to note that nonlinear diffusion exhibits some very peculiar and unexpected features. For instance, having two identical specimens drying in environments of different humidities, the time needed to reach a certain humidity in the core may be greater for the specimen which is in the environment of lower humidity. This phenomenon, which could never happen for linear diffusion, may be intuitively explained by the fact that the surface region which dries up quicker attains a lower permeability and thus in effect hinders more strongly further loss of water from the core.

#### Conclusions

Diffusion coefficient  $C$  for drying of concrete strongly decreases when passing from pore humidity 0.9 to 0.6 while below 0.6 it is approximately constant (Fig. 3). The dependence of  $C$  upon  $H$  may be approximately expressed by the empirical equation (9), in which  $H_c \approx 0.75$ ,  $\alpha_0 \approx 0.03$  to 0.10,  $n = 6$  to 16,  $C_1 = 0.1$  to 0.5  $\text{cm}^2/\text{day}$  for typical dense concretes of low water-cement ratios. The nonlinear diffusion theory gives a far better prediction of drying of concrete than does the linear theory used in the past.

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#### Appendix - Basic Notations

- $C, C_1$  = diffusion coefficient (Eqs. 1 and 3) and its value at  $H = 1$ ;
- $H, H_{en}, H_c$  = pore humidity (relative vapor pressure), environmental humidity and parameter in Eq. (9);
- $L$  = half-thickness of slab;
- $n$  = exponent in Eq. (9);
- $r$  = radius coordinate of a cylinder or sphere;
- $R$  = radius of cylinder or sphere;
- $t, t_0$  = time, and instant of exposure to drying environment;
- $w$  = mass of water in a unit volume of material;
- $x$  = coordinate across the thickness of slab;
- $\alpha_0$  = parameter in Eq. (9);
- Prime as in  $t', x', H'$  stands for non-dimensional variables, Eq. (7).

#### Appendix - Note on Dependence of C on Time

As has been noted in the introductory paragraph, the dependence of  $C$  upon the drying period of specimen (15),  $t-t_0$ , is not satisfactory from the fundamental point of view. Namely, this dependence would mean that  $C$  depends on some physico-chemical process which changes the material properties and is caused by the drop in water content. Since this drop is non-uniform throughout the specimen, such a process would have to be progressing faster near the surface than in the core. Therefore, the drying period on which  $C$  depends would have to be taken different in every point of the specimen and, especially, in the surface and core regions. Nevertheless, the dependence of  $C$  upon  $t-t_0$  has served as a practically useful empirical formulation allowing considerable improvement in the prediction of drying (within a certain range of thicknesses), as Pickett has clearly demonstrated in his papers. Finally, it should be noted that, as far as the effect of hydration (aging) in young concrete is concerned, dependence on time (or, more correctly, the equivalent hydration period (6)) must be considered. But the effect of aging has not been investigated in this paper.