

# Moisture and Heat Transport With Particular Reference to Concrete

T. Z. HARMATHY, Division of Building Research,  
National Research Council of Canada

Over the years three theories have gained general acceptance in explaining the movement of moisture in porous media: the diffusion theory, the capillary flow theory, and the evaporation-condensation theory. Because a wet porous solid actually consists of at least three phases, the mechanism of simultaneous moisture and heat transport is very complex. During the capillary and funicular states of the system, moisture moves primarily by a convective transport mechanism, and the rate of moisture movement is relatively insensitive to the properties of the solid matrix. In the pendular state, the evaporation-condensation mechanism is predominant, and the rate of moisture migration depends on the complexity of the pore structure. For fresh concretes the related problems are augmented by the hydration reactions.

•FOR several decades soil scientists and chemical engineers have shown considerable interest in the problem of moisture migration in porous media. Soil scientists have been primarily concerned with the movement of moisture at relatively high pore saturations and have developed rather complex mathematical models to describe the process under both isothermal and non-isothermal conditions. Chemical engineers, being mainly interested in industrial drying operations, have paid considerably more attention to the effect of certain characteristics of the surroundings on the variation of total moisture content within the boundaries of the drying solid than to the internal mechanism of moisture migration.

## DIFFUSION AND CAPILLARY FLOW THEORIES

Over the years several explanations have been offered for the migration of moisture in porous media. Three deserve detailed discussion: the diffusion theory, the capillary flow theory, and the evaporation-condensation theory. Symbols used in the equations that follow are defined at the end of the paper.

The movement of moisture by diffusion was proposed as the principal flow mechanism by Lewis (1), Tuttle (2), Sherwood (3), Newman (4), Childs (5), Kamei (6), and many others. The diffusion theory is based on the assumption that the moisture flux is proportional to the gradient of moisture concentration. For one-dimensional moisture flow

$$n = -\rho_m \times \frac{\partial m}{\partial x} \quad (1)$$

where  $x$  is assumed to depend only on some characteristics of the porous medium.

By combining Eq. 1 with the equation of continuity (7)

$$\rho_m \frac{\partial m}{\partial t} + \frac{\partial n}{\partial x} = 0 \quad (2)$$

Fick's second law is obtained

$$\frac{\partial m}{\partial t} = \kappa \frac{\partial^2 m}{\partial x^2} \quad (3)$$

which is formally identical to Fourier's law of heat conduction.

The inadequacy of the diffusion theory in describing the migration of moisture was pointed out by McCready and McCabe (8) and discussed in detail by Hougen and co-workers (9). Although a group of research workers attempted to achieve better agreement between theoretical and experimental data by regarding the diffusion coefficient,  $\kappa$ , as a function of moisture concentration,  $m$ , rather than constant, the search continued for the development of more accurate theories.

The fundamentals of the capillary flow theory were laid down by Buckingham (10) in 1907. Since that time the theory has undergone considerable change, initiated by Gardiner (11), Israelson (12), Edlefsen and Anderson (13), and others. In its latest version it is based on the assumption that the following relation exists between moisture flux and the gradient of the "total moisture potential,"  $\Phi$ ,

$$n = -\rho_m K \frac{\partial \Phi}{\partial x} \quad (4)$$

where  $K$ , capillary conductivity, is not a constant but a function of moisture concentration.

Equation 4 is often referred to as Darcy's equation for unsaturated capillary flow. In it, as Edlefsen and Anderson (13) pointed out, the total moisture potential is identical to the partial specific Gibbs free energy (chemical potential) of the moisture in the porous medium, and can be expressed as

$$\Phi = gz + \Psi \quad (5)$$

where  $\Psi$ , the capillary potential, is also a function of the moisture concentration. In problems connected with soil moisture, the level of the water table is taken as the  $z = 0$  level.

By combining Eqs. 4 and 5 with the equation of continuity, Eq. 2, the following equation is obtained for horizontal flow:

$$\frac{\partial m}{\partial t} = \frac{\partial}{\partial x} \left( \kappa \frac{\partial m}{\partial x} \right) \quad (6)$$

where  $\kappa$ , the coefficient of capillary diffusion, is defined as

$$\kappa = K \frac{\partial \Psi}{\partial m} \quad (7)$$

Equation 6 can be recognized as a modified form of Fick's second law of diffusion with a diffusion coefficient dependent on moisture concentration.

Before solving Eq. 6, the  $K = K(m)$  and  $\Psi = \Psi(m)$  functions must be determined experimentally for the porous medium of interest. The nature of these functions has been studied by Richards (14), Philip (15), Schofield (16), and many others.

The capillary flow theory was further modified by Philip (17, 18, 19), Philip and de Vries (20), and de Vries (21) to include movement of water in the gaseous phase (in the pores of the solid), in the "adsorbed" phase, and under the effect of temperature gradient. These workers also added a second equation to the basic equation of capillary flow (Eq. 6 for horizontal flow) in order to balance the energy changes brought about by the movement and evaporation of moisture. Krischer in Germany (22, 23) and Lykov's school in Russia (24, 25), based on somewhat different reasonings, developed sets of equations closely resembling those of Philip and de Vries.

Chemical engineers applied the capillary flow theory in a different way. Based on the fundamental work of Haines (26), Ceaglske and Hougen (27), Pearse and co-workers (28), and Corben and Newitt (29) derived an expression for the moisture flux by balancing the capillary and gravitational forces, acting on a thread of water in the pores, against the frictional forces.

Before discussing the evaporation-condensation theory, it is desirable to examine briefly some common characteristics of wet porous solids and to discuss experimental findings concerning an important moisture and heat transport process—namely, drying.

### THE POROUS SYSTEM

Difficulties in understanding the mechanism of moisture movement in porous solids were probably the result of inaccurate modeling of the system in which the moisture movement takes place. Many research workers assumed directly or implied by the use of certain laws (e.g., Eq. 1 for diffusion) that a porous solid is a single-phase system. In reality, a wet solid consists of at least three phases: (a) a solid phase, i.e., the material of the porous matrix; (b) a liquid (or absorbed) phase, which is essentially water; and (c) a gaseous phase, a mixture of air and water vapor. (Air can be regarded as a single component of the system.) The latter two are contained within the visible boundaries of the first. This three-phase system will be referred to hereafter as porous system for brevity.

In most practical problems it is permissible to regard the solid phase as a single-component, rigid material containing a network of interconnected pores and exhibiting, in macroscopic dimensions, isotropic characteristics.

The water in the liquid phase of the porous system is, to some extent, different from ordinary liquid water. In a few layers adjoining the pore surface, the water molecules are tightly held by a force field. These adsorbed molecules have very limited mobility and can move only by molecular transport processes, in other words, past each other on a molecular scale.

Outside the adsorbed layers the liquid water behaves more like water in narrow capillary tubes. This portion of the liquid phase, commonly referred to as capillary water, has a high degree of mobility. For this water, convection is the primary transport mechanism; that is, the molecules can move relatively freely in larger masses on a macroscopic scale.

In the gaseous phase, air and water molecules can move past each other by some molecular transport mechanism, mainly diffusion. In addition, the air and water molecules also move together in large masses, usually under the effect of pressure gradients.

It becomes obvious that because of the complexity of the system the diffusion theory cannot describe correctly the total moisture migration.

### EQUILIBRIUM SORPTION RELATION

The water vapor concentration in the gaseous phase is generally not far removed from a value corresponding to the equilibrium sorption relation, which is an experimentally developed relation between the amount of liquid phase moisture,  $m$  (sometimes expressed in terms of relative saturation,  $m/\epsilon$ ), and the equilibrium vapor pressure,  $P_V$  (usually expressed in terms of the relative humidity in an equilibrium environment,  $P_V/P_V^0$ ). (In equilibrium, the partial pressure of water vapor,  $P_V$ , is the same in the environment as in the porous system.) The sorption relation depends on certain characteristics of the porous system. Three factors are of major importance: (a) the porosity of the solid matrix,  $\epsilon$ , which determines the maximum amount of moisture that the solid can hold; (b) the specific surface,  $s$  (i.e., the magnitude of the internal pore surfaces per unit volume of the matrix), which determines the maximum amount of moisture that the solid can hold by adsorption; and (c) a constant,  $C$ , in the Brunauer-Emmett-Teller equation (30), which characterizes the affinity between the pore surfaces and the water molecules.

The sorption relation is normally obtained by experiment, although if  $\epsilon$ ,  $s$ , and  $C$  are known it is possible to obtain at least a rough estimate of it (31).

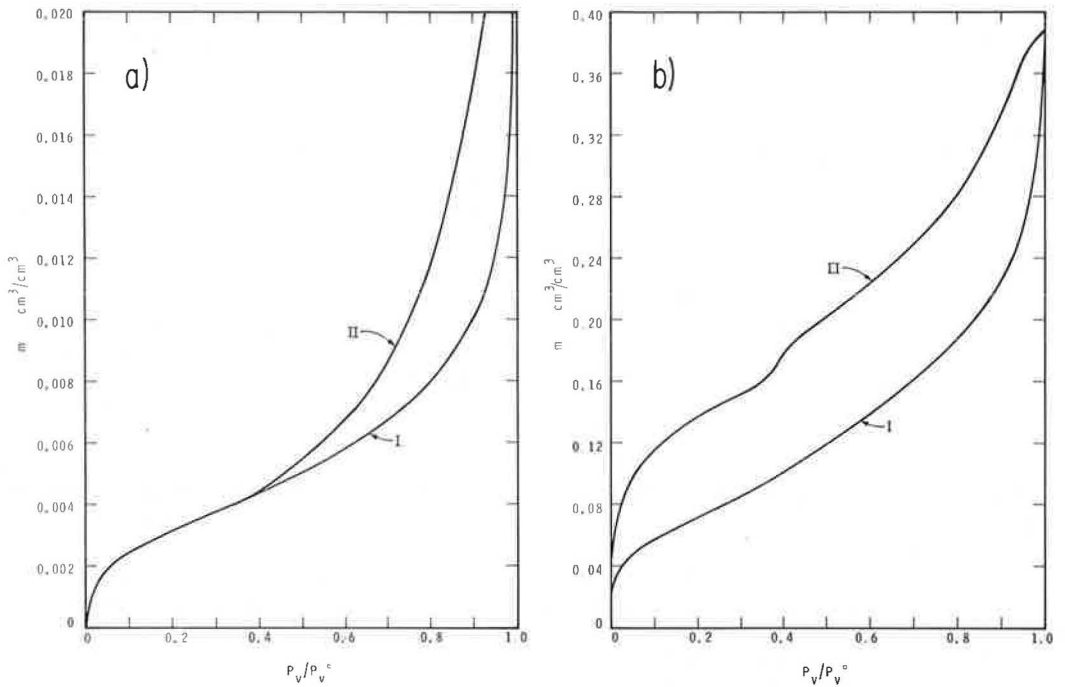


Figure 1. Sorption equilibria: (a) clay brick, (b) hydrated cement paste; curve I, adsorption; curve II, desorption.

Figure 1 shows the sorption relations for two building materials, a clay brick and a hydrated cement paste. The sorption relation for both materials is characterized by two curves, an adsorption curve obtained by a monotonic increase of the vapor pressure of the ambient air from 0 to  $P_v^0$  through very small equilibrium steps, and a desorption curve obtained by the reverse procedure. (These curves are, to some degree, also dependent on the temperature, and therefore have to be obtained while keeping the temperature constant. For this reason they are often referred to as sorption isotherms.) Any point within the hysteresis loop formed by the two curves may represent an equilibrium condition for the system. The uncertainty concerning the effective equilibrium sorption relation presents difficulties in the rigorous treatment of moisture migration problems.

The sorption relation for clay brick (Fig. 1a) is a type commonly met among inorganic solids. The sorption hysteresis in the  $0.4 < P_v/P_v^0 < 1$  interval is caused by capillary water. The geometry of the surfaces of capillary water, determined by moisture concentration, controls (but not uniquely) the equilibrium vapor pressure in the pores by virtue of the Kelvin equation (32). In the  $0 < P_v/P_v^0 < 0.4$  interval the water molecules are held mainly by adsorption on the pore surfaces, and the sorption relation is uniquely determined by the specific surface,  $s$ , and the constant,  $C$ .

For hydrated cement paste (Fig. 1b) the hysteresis loop extends over the entire  $0 < P_v/P_v^0 < 1$  domain. The hysteresis in the  $0 < P_v/P_v^0 < 0.4$  interval is attributed to certain irreversible phenomena of a non-adsorptive nature (33). By comparing Figure 1a and 1b it may be seen that cement paste holds a much larger amount of moisture in equilibrium with any environment than does clay brick. For this reason it is usual to refer to cement paste and similar materials as hygroscopic materials.

If the porosity and specific surface of the porous matrix are known, it is possible, using the Kozeny equation (34), to make a rough estimate of the permeability of the matrix, which also plays some part in the process of moisture migration (as mentioned later).

## DRYING

Drying is probably the most common process in which simultaneous moisture and heat transport play a dominant role. To gain insight into some practical aspect of moisture migration it seems desirable to review briefly the present state of knowledge concerning drying. For simplicity, the drying of a slab is discussed in an environment of constant temperature and relative humidity.

If the relative pore saturation is initially high, the average moisture content of the slab will decrease fairly fast during the first period of drying (Fig. 2a). This period is usually referred to as the constant rate period. Drying proceeds at an approximately constant rate roughly equal to the rate of evaporation from a free-water surface under identical environmental conditions. The temperature of the slab also is approximately constant (Fig. 2a) and, provided drying takes place in a fast airstream, is equal to the wet bulb temperature of the ambient air.

The first three curves in Figure 2b show the moisture distribution in the slab during the constant rate period. The relatively small gradients of moisture concentration clearly indicate that at this stage convection (capillary flow) is the principal mechanism of migration. From the previously mentioned finding concerning the rate of drying, it is obvious that the evaporation of moisture takes place almost entirely at the surfaces of the slab.

Convective movement of moisture (i.e., the capillary flow mechanism) is limited to conditions of the porous system in which continuous water threads exist in the pores, namely, to the capillary and funicular states of the system (26, 27). As the amount of moisture in the pores decreases, the water threads gradually break up and a so-called pendular state is reached. The central cores of the pore channels are now occupied by the gaseous phase, and a still small but steadily increasing portion of the liquid phase moisture is held by adsorption on the pore surfaces. In this state the liquid moisture has a much lower degree of mobility, so that an increasingly larger fraction of the moisture migration takes place in the gaseous phase, partly by molecular transport phenomena (mainly diffusion) and partly by convection induced by pressure gradients.

This transport of moisture in the gaseous phase is possible only if the liquid moisture is first vaporized. Because some of the vaporized water often recondenses in some other zone of the porous system, it is usual to refer to this rather complex

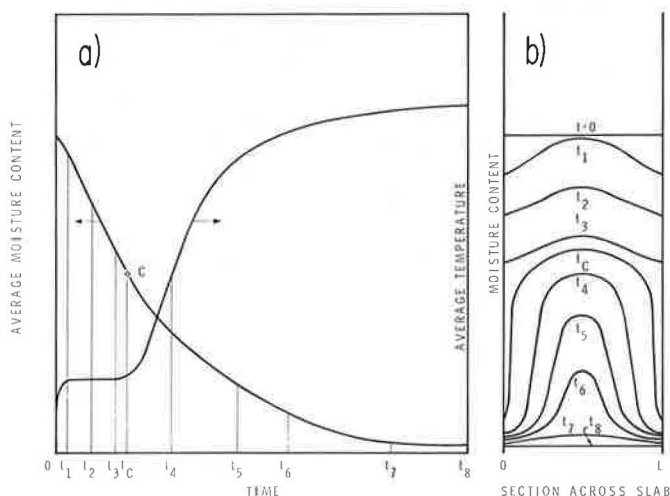


Figure 2. Characteristic curves of a drying porous slab: (a) average moisture content and temperature, (b) moisture distribution.

moisture transport mechanism as the evaporation-condensation mechanism. In it the equilibrium sorption relation, which controls the concentration of water molecules in the gaseous phase, plays an important part.

The constant rate period ends at the so-called "critical point" of drying, where the temperature of the slab takes a sharp upward trend. The moisture distribution at this point is an important characteristic of the pore structure (32).

After a brief transient period, during which the capillary flow mechanism still plays some role in moisture migration, the falling rate period sets in, characterized by the predominance of the evaporation-condensation mechanism. Figure 2a shows the generally steady decrease in the rate of temperature rise during this period, until finally the porous system attains equilibrium with its surroundings and all moisture and heat transport come to an end.

The curves in the lower part of Figure 2b shows various phases of the moisture distribution in the porous slab during the falling rate period. They indicate that the planes at which the bulk of moisture evaporation takes place gradually retreat from the surfaces toward the central plane of the slab, while the moisture concentration at the central plane remains high for a relatively long period.

Clearly, the larger the area of the internal pore surfaces in relation to pore volume, the larger is the portion of moisture retained at the onset of the pendular state and, in turn, the more significant is the evaporation-condensation mechanism in relation to the capillary flow mechanism. Because the rate of drying during the constant rate (or capillary moisture migration) period is relatively high and easily calculable, even without exact knowledge of the laws of capillary flow, the progress of drying during the falling rate period has long been the primary target for research and speculation among chemical engineers.

### EVAPORATION-CONDENSATION THEORY

The evaporation-condensation theory has sprung from the desire to explain the movement of moisture in porous systems under the effect of temperature gradients. It was probably Bouyoucos (35) who first pointed out that in a closed system moisture moves opposite the temperature gradient. Many years later Vassilou and White (36) and Paxton and Hutcheon (37) demonstrated the importance of the equilibrium sorption relation in the moisture transport process. The dominant role of the evaporation-condensation mechanism when moisture moves under the effect of temperature gradient was further discussed by Gurr and co-workers (38), Hutcheon (39), and Kuzmak and Sereda (40).

By adopting simplifying assumptions concerning the porous system and the transport process, it is possible to describe mathematically the combined moisture and heat transport in porous media by the evaporation-condensation mechanism (32, 41). For the porous system the following assumption can be introduced: Although a porous system is in reality a three-phase system, the phases are so finely distributed that from a macroscopic standpoint it can be regarded as a quasi-one-phase system. This assumption implies, on the one hand, that it is possible to assign local values to the concentration of all components and all state variables of the system; and, on the other hand, that even though the system as a whole is generally a non-equilibrium system there is local equilibrium within each sufficiently small element of it. In this way the equilibrium sorption relation is automatically satisfied at each point of the system.

With respect to the transport process, the problem may be greatly simplified if it is assumed that the liquid phase is completely immobile; that is, that the water molecules must first be vaporized before they can move from one point to another in the system. As discussed earlier, for the pendular state of the system (or for the falling rate period of drying) this is a perfectly reasonable assumption.

With the aid of these assumptions and a few well-known principles, such as the laws of conservation of matter and energy, Darcy's law of convective mass transport through porous media (42), Fick's law of diffusion, and Fourier's law of heat conduction, a set of three basic equations will finally be obtained. For one-dimensional moisture and heat flow in a slab of thickness,  $L$ , these equations (41) are of the form



$$\begin{aligned}
& A_k \frac{\partial^2 \varphi}{\partial x^2} + B_k \frac{\partial^2 P}{\partial x^2} + C_k \frac{\partial^2 T}{\partial x^2} + D_k \left( \frac{\partial \varphi}{\partial x} \right)^2 + E_k \left( \frac{\partial P}{\partial x} \right)^2 + F_k \left( \frac{\partial T}{\partial x} \right)^2 \\
& + G_k \frac{\partial \varphi}{\partial x} \frac{\partial P}{\partial x} + H_k \frac{\partial \varphi}{\partial x} \frac{\partial T}{\partial x} + J_k \frac{\partial P}{\partial x} \frac{\partial T}{\partial x} = K_k \frac{\partial \varphi}{\partial t} + L_k \frac{\partial P}{\partial t} + M_k \frac{\partial T}{\partial t} \quad (k = 1, 2, 3)
\end{aligned} \tag{8}$$

The most commonly applicable boundary conditions are as follows:

$$\left. \begin{aligned} \frac{\partial \varphi}{\partial x} &= (-1)^{l+1} \nu \alpha \left( \frac{RT}{PD} \right) (\varphi - \varphi_{\infty l}) \end{aligned} \right\} \quad \begin{aligned} l &= 1 \text{ at } x = 0 \\ l &= 2 \text{ at } x = L \end{aligned} \tag{9}$$

$$\left. \begin{aligned} \frac{\partial T}{\partial x} &= (-1)^{l+1} \frac{h}{k} (T - T_{\infty l}) \end{aligned} \right\} \tag{10}$$

$$P = P_{\infty l} \tag{11}$$

When solved, these equations, together with the appropriate initial conditions

$$\varphi = \varphi(x, 0), \quad T = T(x, 0), \quad P = P(x, 0) \quad 0 \leq x \leq L \tag{12}$$

yield the complete moisture concentration, temperature, and pressure history of the wet porous slab in any transient process, provided that the system is in its pendular state.

For practical reasons,  $\varphi$ , the concentration of water vapor in the gaseous phase, has been selected as one of the three independent state variables of the system. This information is usually of no direct practical interest. It is used to calculate the moisture concentration history of the system by utilizing the equilibrium sorption relation, which is in fact a relation between  $m$  and  $\varphi$  ( $=P_v/P$ ).

Some of the coefficients  $A_1 \dots M_3$  are equal to zero. Others are, in general, functions of (a) the three state variables,  $\varphi$ ,  $P$ , and  $T$ , and (b) the following material characteristics: specific heat of all components, density of all components, thermal conductivity of all components, porosity and permeability of the solid matrix, coefficient of diffusion of water vapor in air, viscosity of gaseous phase, equilibrium sorption relation, and heat of sorption.

Figure 3 shows the computed moisture concentration, temperature and pressure history of a 1-cm thick brick slab in a drying process.

Equations 8 to 12 can be solved only with high-speed computers. It is possible, however, to draw a few conclusions concerning the rate of moisture movement in a porous system, either simply from some characteristics of the solid or from an exploratory drying test carried out on a thin slab cut from the solid.

### SOME FACTORS AFFECTING THE RATE OF MOISTURE MIGRATION

During the capillary and funicular states of the porous system (i.e., at relatively high pore saturations), the rate of moisture movement is relatively insensitive to the properties of the system and depends mainly on external factors such as temperature and water vapor concentration of the ambient air and on air velocity, which affects the coefficients of heat and mass transfer at the surfaces.

These transfer coefficients continue to play some part in the moisture migration process, even during the pendular state (i.e., during the falling rate period of drying). Nevertheless, at this state the internal characteristics of the system become of primary importance. Because liquid moisture has to be vaporized to move from one location to another and because the heat of desorption is obtained by conduction from the surface of the system, it is clear that, other conditions being equal, moisture migration in a drying process is faster if the solid matrix is of a higher thermal conductivity.

One can also expect that the rate of moisture migration will be higher in solids of relatively simply pore structure. The simplicity of the pore structure is characterized

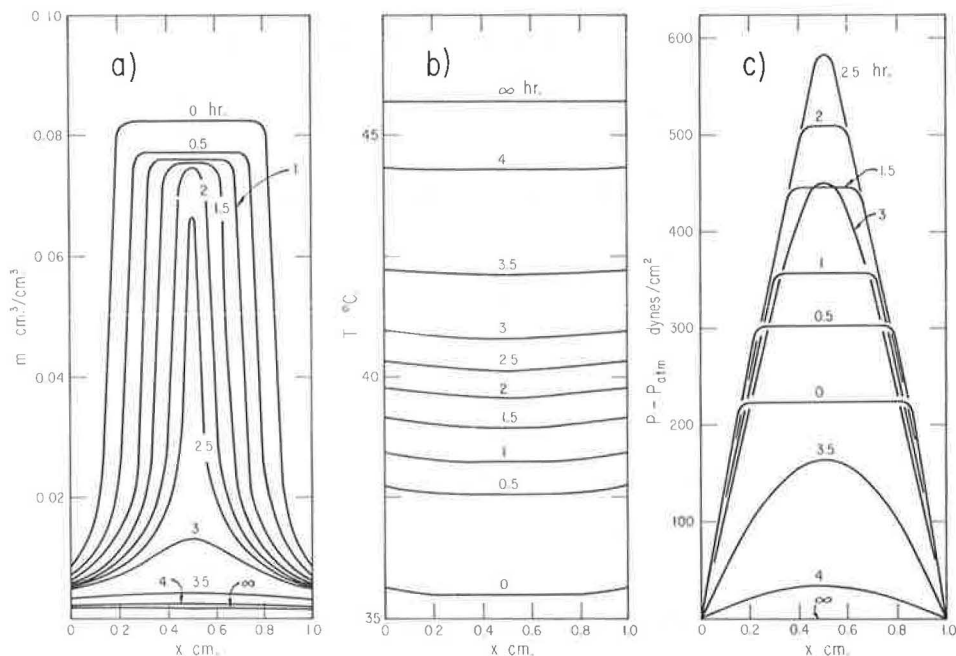


Figure 3. Computed distribution curves in simulation of a falling rate drying process (41).

by low values of the specific surface [by virtue of the previously mentioned Kozeny equation (32, 34) these also imply high permeabilities] and, in turn, by low equilibrium moisture concentrations, as reflected by the adsorption and desorption isotherms over the  $0 < P_v/P_v^0 < 0.9$  interval (Fig. 1a). Because such solids contain relatively small amounts of moisture at the critical point and retain very little residual moisture at the end of a drying process, one may presume that the moisture content at the critical point and the moisture retention of an exploratory slab specimen at the completion of the drying test are rough measures of the "resistance" of the solid matrix to moisture movement during the pendular state. (The residual moisture concentration is usually represented by a point within the hysteresis loop at a value of  $P_v/P_v^0$  equal to the relative humidity of the environment.)

Figure 4 shows the results of drying tests performed under identical environmental conditions on five 1-cm thick slabs: a hydrated portland cement paste, two lightweight concretes, one autoclaved normal weight concrete, and a clay brick. The drying curves have been slightly displaced along the time axis in order to have the critical points line up at 0.5 hour. Information concerning the materials is given in Table 1.

Figure 4 shows clearly that the rate of drying during the constant rate period depends very little on the characteristics of the system. The figure also confirms the previously discussed principles concerning the rate of moisture movement during the falling rate period.

#### EFFECT OF MOISTURE CONTENT ON THERMAL CONDUCTIVITY

Very often, only the heat transport process is of practical interest in a process of simultaneous moisture and heat transport. It has always seemed very attractive, therefore, to reduce the complex problem of heat and moisture transport to a problem of heat conduction in a medium with a thermal conductivity dependent on the moisture concentration. In achieving this, many research workers have assumed that the thermal conductivity of the moist solid is always higher than that of the dry solid.



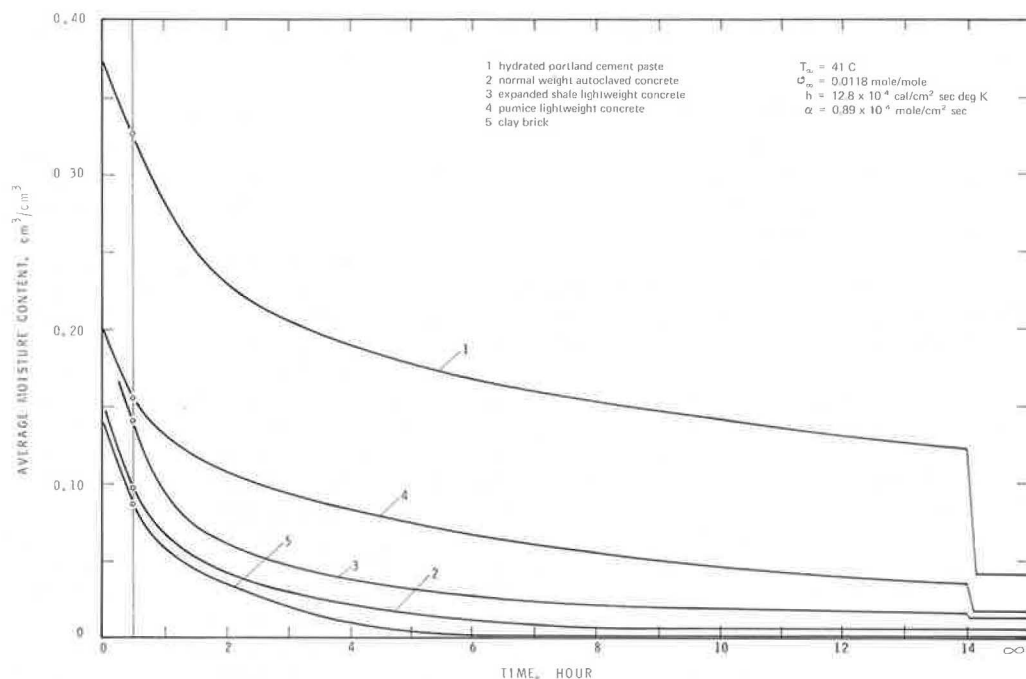


Figure 4. Drying experiments performed on 1-cm thick slabs.

TABLE 1  
INFORMATION CONCERNING MATERIALS IN FIGURE 4

Material	Density (g/cm <sup>3</sup> )	Thermal Conductivity (cal/cm sec deg K)	Porosity (cm <sup>3</sup> /cm <sup>3</sup> )	Specific Surface <sup>a</sup> (cm <sup>2</sup> /cm <sup>3</sup> )
Hydrated portland cement	1.53	0.0014	0.43	220 × 10 <sup>4</sup>
Normal weight concrete autoclaved	2.05	0.0027	0.24	10 × 10 <sup>4</sup>
Lightweight concrete 1, expanded shale	1.22	0.0010	0.34	90 × 10 <sup>4</sup>
Lightweight concrete 2, pumice	1.23	0.0010	0.39	
Clay brick	1.98	0.0025	0.26	10 <sup>4</sup>

<sup>a</sup>Estimated with assistance from Harmathy (31).

Cammerer (43) expressed the increase in the thermal conductivity as a unique function of the moisture concentration. There is a special case, that of steady-state heat conduction occurring during the capillary state, in which moisture in the porous solid can be regarded simply as a factor influencing the apparent value of thermal conductivity; and this value can be expressed as a function of moisture concentration (44).

Unfortunately, the concept of thermal conductivity as well-defined function of moisture concentration is not applicable to other conditions. In fact, even the assumption that thermal conductivity increases with increasing moisture concentration is questionable. If moisture flow takes a direction opposite that of heat flow, as is generally the

case in drying processes, the apparent value of the thermal conductivity of a solid in a moist condition is usually lower than that in the dry condition.

## MOISTURE AND HEAT TRANSPORT IN CONCRETE

Although all that has been said in the previous sections about simultaneous moisture and heat transport in porous systems is applicable to concrete, concrete (or more specifically hydrated cement paste) has certain characteristics that make it different from most other inorganic porous materials.

A major portion of portland cement paste consists of an impure calcium silicate hydrate of somewhat indefinite composition, usually referred to as tobermorite gel. (There are some indications that it may not be entirely correct to regard portland cement paste as a gel.). This material has a very complex microstructure. It exhibits a specific surface that is unusually large among inorganic materials and surpassed only by industrial adsorbents. Consequently, portland cement paste can hold a substantial amount of moisture in equilibrium with a normal atmospheric environment (Fig. 1b). This implies that the critical point appears very early in the drying process, and that in the pendular state the moisture migration in cement paste is very slow. Figure 4 indicates the slowness of moisture migration in cement paste in comparison with that in a few other building materials. Although the thickness of the specimens was very small (1 cm), the temperature of the drying cabinet fairly high (41 C), and the water vapor concentration in the cabinet low, it took several days for the hydrated cement paste specimen to attain equilibrium with its surroundings.

Slowness of moisture movement in concrete, which sometimes appears to be a nuisance in technical problems, is more often a fortunate circumstance. Because of it, large concrete masses are capable of holding substantial amounts of capillary water in their central cores for long periods following placement, even under normal atmospheric conditions. Capillary water is essential for the hydration reactions that develop very slowly, often over several years. If the bulk of this capillary water is removed too early by the application of forced drying, the hydration reactions may stop completely (45) and the quality of the concrete suffers.

As one could expect by virtue of the Kozeny equation (32, 34), permeability of cement paste is very low. Because of this, high pressure gradients may develop in concrete structures if, in their capillary state, they are exposed to a sudden temperature rise. Under certain circumstances these pressure gradients may result in explosive spalling (46).

From a practical point of view, the progress of drying of concrete masses following placement is of particular interest, but unfortunately it is the most difficult to follow. Even for fully mature cement pastes, the capturing of water molecules by the solid matrix is not a simple surface phenomenon (adsorption). This fact always poses extra difficulties in defining sorption equilibria.

With fresh concretes the difficulties are augmented by the hydration reactions that continuously change the characteristics of the solid matrix and deplete the moisture participating in migration. Thus, for some time to come research workers concerned with the migration of moisture in fresh concrete structures will have to rely more on exploratory tests than on theoretical predictions.

## NOMENCLATURE

The following symbols are used in the equations. Some symbols used as coefficients in Eq. 8 are not listed.

- C = constant in the Brunauer-Emmitt-Teller equation, dimensionless;
- D = effective coefficient of diffusion of water vapor in air inside a porous medium,  $\text{cm}^2/\text{sec}$ ;
- g = gravitational acceleration,  $\text{cm}/\text{sec}^2$ ;
- h = heat transfer coefficient,  $\text{cal}/\text{cm}^2 \text{ sec deg K}$ ;
- k = thermal conductivity of the porous system  $\text{cal}/\text{cm sec deg K}$ ;
- K = capillary conductivity, sec;

- $l = 1, 2$ ;  
 $L$  = thickness of slab, cm;  
 $m$  = volumetric moisture concentration,  $\text{cm}^3/\text{cm}^3$ ;  
 $n$  = moisture flux,  $\text{g}/\text{cm}^2 \text{ sec}$ ;  
 $P$  = total pressure,  $\text{g}/\text{cm sec}^2$  (= dyne/ $\text{cm}^2$ );  
 $P_v$  = equilibrium vapor pressure in the pores; partial pressure of water vapor in the environment,  $\text{g}/\text{cm sec}^2$ ;  
 $P_v^0$  = equilibrium vapor pressure for free water,  $\text{g}/\text{cm sec}^2$ ;  
 $R$  = gas constant,  $\text{g cm}^2/\text{sec}^2 \text{ deg K mole}$ ;  
 $s$  = specific surface,  $\text{cm}^2/\text{cm}^3$ ;  
 $t$  = time, sec (if not otherwise stated);  
 $T$  = temperature, deg K (if not otherwise stated);  
 $x$  = coordinate (horizontal), cm;  
 $z$  = coordinate (vertical), cm;  
 $\alpha$  = mass transfer coefficient,  $\text{mole}/\text{cm}^2 \text{ sec}$ ;  
 $\epsilon$  = porosity,  $\text{cm}^3/\text{cm}^3$ ;  
 $\kappa$  = coefficient of capillary diffusion,  $\text{cm}^2/\text{sec}$ ;  
 $\nu$  = empirical factor, dimensionless;  
 $\rho$  = bulk density of solid matrix,  $\text{g}/\text{cm}^3$ ;  
 $\rho_m$  = density of moisture,  $\text{g}/\text{cm}^3$ ;  
 $\Phi$  = total moisture potential,  $\text{cm}^2/\text{sec}^2$ ;  
 $\phi$  = mole fraction of water vapor in the gaseous phase, mole/mole;  
 $\chi$  = coefficient of diffusion of moisture,  $\text{cm}^2/\text{sec}$ ;  
 $\Psi$  = capillary potential,  $\text{cm}^2/\text{sec}^2$ ;  
atm = atmospheric;  
 $k = 1, 2, 3$ ; and  
 $\infty$  = of the ambient air.

#### ACKNOWLEDGMENT

The cooperation of E. Oracheski in the experimental work is greatly appreciated.

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