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MOISTURE EQUILIBRIUM AND MIGRATION IN
BUILDING MATERIALS

ANALYZED

BY

P. J. SEREDA AND N. B. HUTCHEON

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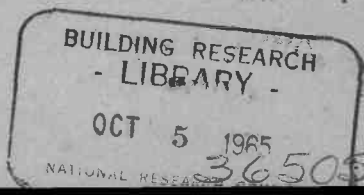
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ÉQUILIBRE ET MIGRATION DE L'HUMIDITÉ DANS LES MATÉRIAUX DE CONSTRUCTION

SOMMAIRE

L'auteur passe en revue les facteurs qui influent sur l'équilibre existant entre la teneur en humidité de divers matériaux de construction et la chaleur et l'humidité ambiantes. Il fait mention de forces, potentiels, énergies, structure des pores, superficie et hystérésis. Il évalue l'utilité du concept de la succion pour des travaux portant sur l'humidité dans des conditions proches de la saturation et il évoque l'intérêt qu'il y aurait à établir un rapport entre l'échelle des suctions et l'humidité relative. La deuxième partie de l'article concerne la migration de l'humidité dans des conditions isothermiques constantes et les complications qui se produisent quand il n'y a pas égalité de température. On mentionne certains travaux importants effectués par d'autres chercheurs dans des domaines où le flux de chaleur et d'humidité a quelque importance.



MOISTURE EQUILIBRIUM AND MIGRATION IN BUILDING MATERIALS

BY P. J. SEREDA¹ AND N. B. HUTCHEON¹

SYNOPSIS

Factors influencing the moisture content of a variety of building materials in equilibrium with their thermal and moisture environments are discussed. Reference is made to forces, potentials, energies, pore structure, surface area, and hysteresis. The usefulness of the suction concept in dealing with moisture at conditions close to saturation and of the relationship of the suction scale to relative humidity is discussed.

The second part of the paper introduces a discussion of moisture migration under isothermal steady-state conditions, and indicates the complications inherent in the nonisothermal case. We refer to some significant work by others in fields where combined heat and moisture flow is of concern.

Moisture is inevitably present as a significant factor in almost all aspects of building performance, including fire exposure. The fire scientist must therefore be interested in the moisture contents that occur in building constructions under various environmental conditions. Some of the basic aspects of moisture equilibrium and moisture migration are reviewed, keeping the interests of the fire scientist in mind.

ADSORPTION OF WATER

It is generally known that an adsorption isotherm represents the equilibrium amount of water held on the surface of a unit weight of a given material at any condition of relative humidity (RH). The theory of adsorption often is not well known and a simple discussion of the theory might give more meaning to

graphic representation and illustrate how this information can be of use to the fire technologist.

This simplified discussion on adsorption is based generally on the multi-molecular theory of Brunauer et al (1).² It is known that water molecules are strongly attracted to the surface of most materials. Because the attraction decreases sharply when water molecules are deposited on other water molecules to build successive layers, it is reasoned that the first (monomolecular) layer will be complete before the second and subsequent layers of water molecules are deposited.

This concept allows for the determination of the point along the isotherm (usually between 0 and 30 per cent RH) when a monomolecular layer is established and the corresponding quantity of water designated as W_m is determined through

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² The boldface numbers in parentheses refer to the list of references appended to this paper.

the application of the BET equation

$$\frac{P/P_0}{W(1 - P/P_0)} = \frac{1}{WmC} + \frac{(C - 1)}{WmC} (P/P_0) \quad (1)$$

where:

W = weight of water (or any gas) adsorbed at vapor pressure P ,

P_0 = saturated vapor pressure at the temperature of the sample, and

C = constant related to the heat of adsorption.

When Wm has been determined, the known value of the water molecule size may be used to arrive at a value for the total surface area of the material in question. Surface area, in this connection, refers to all the surface which water molecules can reach; for most porous

isotherm between 50 and 100 per cent RH. The relationship between the vapor pressure over the meniscus of a liquid in a capillary compared to the bulk liquid is given by the Kelvin equation

$$\ln P/P_0 = \frac{-2\gamma V}{rRT} \quad (2)$$

where:

P = vapor pressure,

γ = surface tension,

V = molar volume of the liquid at absolute temperature, T ,

R = gas constant, and

r = radius of curvature of the liquid in the capillary; thus, capillaries of the smallest radii fill at the lowest pressures.

TABLE 1—THE RELATIONSHIPS BETWEEN RELATIVE VAPOR PRESSURE, RADIUS OF CURVATURE OF MENISCUS, EQUIVALENT COLUMN OF WATER, AND pF .

P/P_0 , %	Radius of Curvature, μ	Height of Column of Water		Schofield's pF
		cm	psi	
0.08	0.000147	10^7	1.42×10^5	7
49.0	0.00147	10^6	1.42×10^4	6
93.0	0.0147	10^5	1.42×10^3	5
99.3	0.147	10^4	1.42×10^2	4
99.9	1.47	10^3	1.42×10	3
99.999	147	10	1.42×10^{-1}	1
100.0	∞	0	0	...

materials this constitutes the large bounding surface for all the micro- and macropores, capillaries, or voids found inside the body of the material.

After a monomolecular layer of water is established, successive layers of water molecules are deposited as the RH is increased. Finally a stage is reached when menisci can form in the fine capillaries and the filling of the pore space is accomplished through a capillary condensation process which is governed by the relationship between the depression of the vapor pressure over the curved surface of the water and the radii of the capillaries. Roughly, this represents the region of the

Because of this relationship it is possible to relate RH to the radius of curvature of the meniscus or radius of the capillary, which in turn can be related to the theoretical height of capillary rise. Thus the potential at which a particular moisture content is held in a porous body may be expressed either in terms of RH, which directly reflects the depression of vapor pressure below that of a flat water surface, or, as was done by Schofield (2), as a negative hydraulic head. The latter, commonly referred to as suction, may be expressed in centimeters, or often more conveniently in Schofield's pF units (log of the negative head in centimeters).

Special use of this concept is made in soil technology as summarized by Penner (3). The various relationships are presented in Table 1.

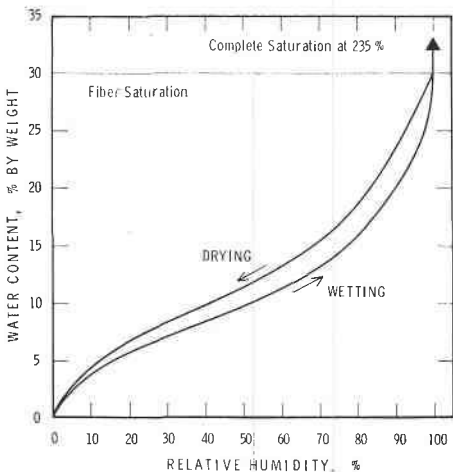


FIG. 1—Equilibrium Moisture Contents for Spruce at 20°C.

When the pores and capillaries in the material are very small (below 0.01μ) an isotherm adequately represents the quantity of water that is held at any RH, from which the surface area and pore size are obtained. Typical isotherms are given for such materials as wood fiber (Fig. 1) and a portland cement paste (Fig. 2a). Such materials are characterized by their large surface area, usually greater than $10^6 \text{ cm}^2/\text{g}$ of material. These and other properties are given by Barkas (4) for wood, Powers and Brownyard (5) for cement, and Van Olphen (6) for clay.

Some materials may, like sand, present a pore system which consists of the interstices between relatively large and nonsorbing grains. Sand retained on 325-mesh screen, having particle diameters greater than 50μ , will have a surface area less than $10^3 \text{ cm}^2/\text{g}$ and practically all the water that will be sorbed will appear

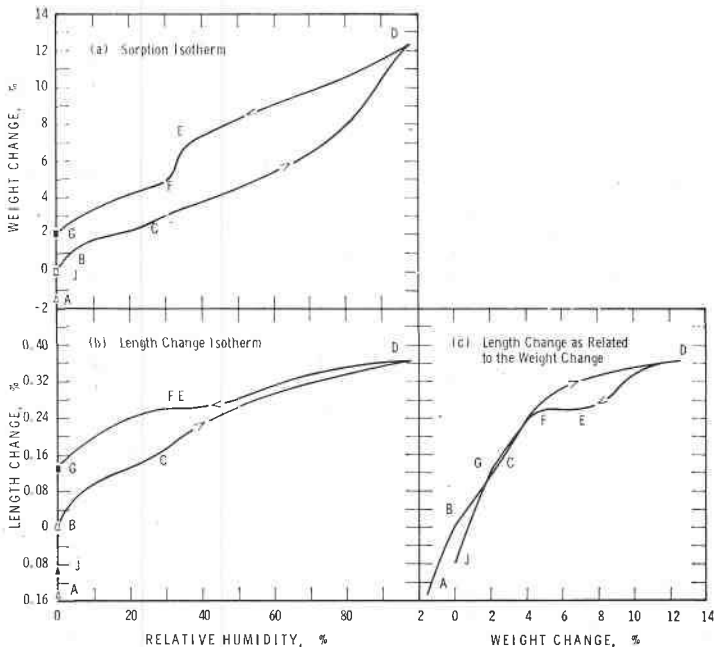


FIG. 2—Compacts of Hydrated Portland Cement.

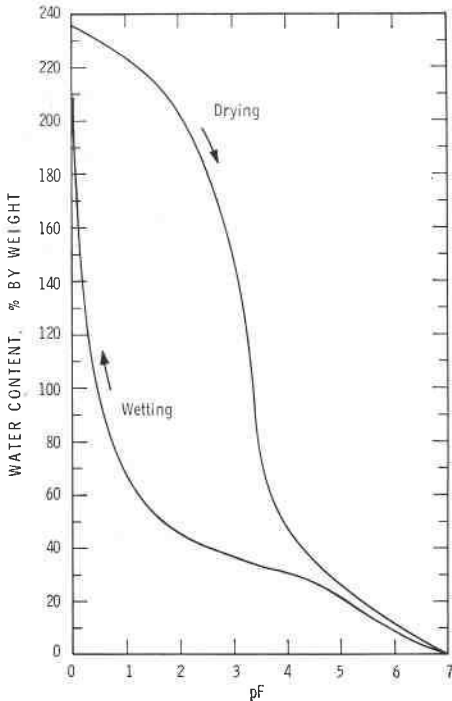


FIG. 3—Suction-Water Content Curves for Spruce at 20 C.

on the isotherm ranging between 99.9 and 100 per cent RH. Because it is not practical to control or measure humidity to the desired sensitivity in this region, the suction concept is specifically applicable to such systems. Conditioning of samples to specific levels of moisture potential can be effected on a porous plate at a potential defined by the negative head as described by Croney et al (7) for the soil system.

There are a number of mixed systems having micro- as well as macroporosity: foamed cellular concrete or natural wood are examples of such systems. The micropore part of these systems, as noted, can be represented by a normal isotherm. However, for the purpose of representing the total water to be removed before the system will be in equilibrium with RH below 99 per cent, it is best to represent it on a basis of suction (Fig. 3 for wood and Fig. 4 for foamed cellular concrete). A foamed cellular concrete consisting essentially of air bubbles in a hardened cement paste presents a micro-

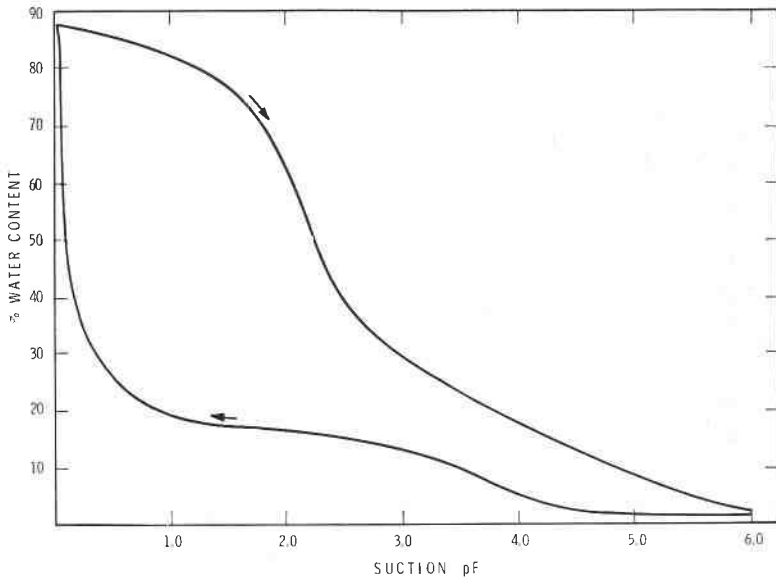


FIG. 4—Suction-Water Content Curves for Foamed Concrete.

pore system characteristic of that paste and a coarse (macro) pore system, not highly connected, represented by the enclosed air bubbles.

Isotherms or moisture content versus suction curves for most materials exhibit a hysteresis in the region from saturation to some intermediate value of moisture content. This means that two different equilibrium values of moisture content may correspond to a single condition of RH or suction, the difference being accounted for only on the basis of the direction of change (prior history). It also means that two materials or two samples of the same material at two different moisture contents, when brought together, may remain at moisture contents differing by the spread between wetting and drying curves.

These characteristics of moisture content in porous systems are of some concern in the drying of materials and measurement of moisture content. Note from Figs. 1 and 3 that wood which is completely saturated can hold more than 200 per cent water by weight (dry basis), yet the moisture content held at $pF = 4$ (99.3 per cent) is only about 40 per cent. Correspondingly, for cellular concrete (Fig. 4), the moisture content at complete saturation is 90 per cent while that at $pF = 4$ is 20 per cent or less, so that 70 per cent moisture content must be removed from a saturated sample before the RH drops below 99.3 per cent. This leads to complications in the use of RH as an index of moisture content at high moisture levels.

DIMENSIONAL CHANGES ACCOMPANYING SORPTION

There exists an imbalance of forces on the surface of a solid giving rise to surface free energy. When water is adsorbed on the surface the net result is a decrease in the free energy and will be reflected in a dimensional change of the units of solid

comprising the body. If the solid has a large surface area then the dimensional change will be correspondingly large.

The relationship of sorbed water to the dimensional change of a number of porous systems has been studied by a number of workers (8-10). These relationships are very useful when considering the mechanical properties of the porous solids. A typical relationship is given in Fig. 2c for cement paste.

The length change versus moisture content change for a given system is unique and characterizes that system. It usually has distinct regions represented by different slopes of the curve and a corresponding different response when a unit moisture content change is experienced. It follows, therefore, that moisture content gradients impose stress gradients on the body and that the magnitude of this stress depends not only on the gradient of moisture content but also on the position along the isotherm. The cracking and checking that occur when drying rapidly large sections of porous materials such as wood and concrete are examples of failure due to stress gradients as the result of moisture content gradients as discussed by Pickett (11). Wood presents a further complication since it is anisotropic with respect to drying shrinkage.

EFFECT OF TEMPERATURE CHANGES

A temperature gradient imposes a stress gradient in a material which may be superimposed, during a fire test, on stress gradients resulting from moisture content gradients. There may be a further interaction between temperature and moisture content since, as Myers (12,13) has shown, the thermal expansion of cement paste varies with moisture content. It is not possible to say, with the present state of knowledge in this field, when the effects are likely to be additive. It seems possible that under fire exposure

on one side of a specimen, the drying shrinkage produced by migration of moisture from the heated face may offset in part the thermal expansion, but the situation is further complicated in the case of concrete by possible differences in both temperature and moisture responses between the cement paste and the aggregate.

EFFECT OF MOISTURE ON STRENGTH

A porous, solid body having a large surface area will experience a large interaction with water as discussed earlier. This interaction usually occurs at the boundaries between units in the system where physical and chemical bonds collectively comprise the strength of the system, and has an influence upon the strength. For a nonhydrate, insoluble system, especially one of large total porosity, there usually is a decrease in strength as water is added, the greatest change being in the region from dry to monomolecular layer equivalent as shown by Dollimore and Gregg (14).

Hydrated porous systems may exhibit many unusual effects because there may be a tendency to dehydrate as the material is exposed to a low vapor pressure. This would undoubtedly have an effect on strength.

We conclude that if the strength of a porous body is affected by moisture content changes, it is quite probable that the fire endurance of such materials may be influenced by the moisture conditioning prior to test. The extent of this influence, however, cannot be predicted because the mechanisms involved are not fully understood.

MOISTURE MIGRATION

The phenomenon of moisture migration is only partially understood, and the associated science has not developed an adequate set of equations describing it. Such equations as those proposed do not

account adequately for all the variables involved, so that the coefficients in them are, of necessity, functions, taking into account the variables which have been disregarded. It seems necessary to suppose from what is known that some variables involving the detailed nature of the porosity, pore size distributions, interconnections between pores, and surface energy effects as they enter into the microdistribution of both thermal and moisture potentials will always be represented by empirical coefficients.

VAPOR DIFFUSION

The equation commonly used to describe water vapor diffusion through materials is based on a form of Fick's law

$$w = -\mu \frac{dp}{dx} \dots \dots \dots (3)$$

where:

w = flow rate per unit area in unit time,

p = vapor pressure,

x = distance along the flow path,

and, hence:

dp/dx = vapor pressure gradient, and

μ = permeability.

Note the close parallel with Fourier's equation for heat flow. The actual transmission of vapor through a material is usually complex, so that coefficient μ is not a simple one, but is actually a function of RH and temperature and may vary along the flow path through the material in question.

Integrating Eq 3 from $x = 0$ to l and from p_1 to p_2 and rearranging, we get

$$w = \bar{\mu} \frac{(p_1 - p_2)}{l} \dots \dots \dots (4)$$

where:

$$\bar{\mu} = \frac{\int_{p_1}^{p_2} \mu dp}{p_1 - p_2}$$

and l = length of flow path, or thickness of material.

When μ is independent of p , then $\bar{\mu}$ is simply μ , but if a functional relationship exists, $\bar{\mu}$ is the average permeability coefficient applicable to the varying conditions along the flow path l , while the coefficient μ is the spot or differential permeability.

The cup or dish method is commonly used for the experimental determination of permeability coefficients (for unit thickness) or of permeance, $\bar{\mu}/l$ (for the thickness stated or implied). Various standard forms and conditions for the dish method are covered in ASTM Method C 355³ and in ASTM E 96.⁴ A discussion of the factors involved in ASTM dish methods was recently presented by Joy and Wilson (15). Application of the results obtained on building materials and their use in estimating moisture migration in building constructions can be found in the ASHRAE Guide and Data Book (16).

A mixed system of units is commonly used in building work. Vapor pressures are expressed in inches of mercury, areas in square feet, time in hours, thicknesses in inches, and weight of vapor in grains. For simplification, a permeance (for the thickness stated or implied) of 1 grain/ft²/hr/in. of mercury has been designated as 1 perm and this practice is now in common use. The corresponding unit of permeability (for unit thickness of 1 in.) is called a perm-inch.

Sheet materials highly resistant to the passage of water vapor, as used in packaging and for vapor barriers in building construction, will have permeances from 0 to 1 perm. Still air has a permeability of 120 perm-in. Most other materials

have permeabilities less than that of still air, with very porous materials such as mineral wool or open fabrics approaching 120 as an upper limit.

The relationship between dry-dish results, (0 per cent one side, 50 per cent RH on the other) and wet-dish results (50 per cent RH one side, 100 per cent RH on the other) are shown for a material such as wood in Fig. 5. Note that the values $\bar{\mu}_1$ and $\bar{\mu}_2$ obtained by substituting the conditions of the respective dish tests

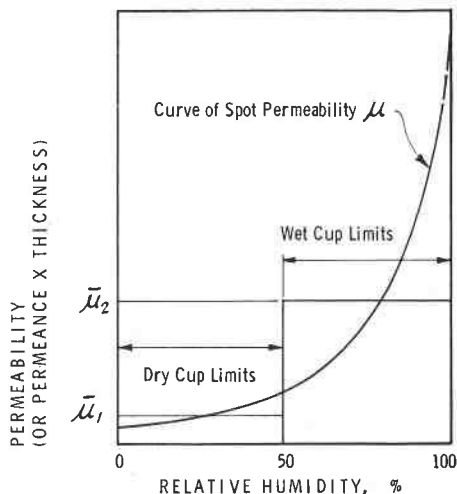


FIG. 5—Relationship between Dry- and Wet-Cup Tests and Spot Permeability for a Material such as Wood.

in Eq 4 are average values applying over the appropriate ranges of RH of the two tests. Since these tests are always carried out at constant temperature there is a direct, linear relationship between vapor pressure and RH.

MOISTURE MIGRATION CHARACTERISTICS

The comparison of dry-dish and wet-dish values for a range of materials suggests three categories: (1) relatively impervious materials which do not show a marked functional relationship between

³ Methods of Test for Water Vapor Transmission of Thick Materials (C 355), 1964 Book of ASTM Standards, Part 14.

⁴ Methods of Test for Water Vapor Transmission of Materials in Sheet Form (E 96), 1964 Book of ASTM Standards, Parts 14, 15, 27, 30.

RH and permeability (dry-dish and wet-dish values the same or nearly so), (2) materials of low to medium permeability which show substantial differences between dry-dish and wet-dish values, often in the ratio of 1:2 or higher, and (3) materials of relatively high permeability which show relatively small increases in wet-dish over dry-dish values.

Many plastic films fall in the first category. It seems reasonable to suppose that they provide a kind of sieve of molecular proportions through which the water molecules must find their way. Barrer (17) has described a mechanism of activated diffusion which is related to the activation energy of the water molecules and can be identified by the temperature effect on permeability

$$\mu = \mu_0 e^{E/RT} \dots \dots \dots (5)$$

There are two possible wet-dish tests. One presents only water vapor at near-saturation to the membrane surface, since there is an air gap between the liquid water in the bottom of the cup and the test membrane above. In the other form, the dish is inverted so that liquid water comes in direct contact with the high-humidity side of the sample. For many materials, there is a marked difference in the results obtained by these two methods, the liquid contact producing higher permeabilities. Many plastic films, however, show little increase when tested in the liquid-contact condition.

Included in the third category will be those materials, such as textiles, porous papers, and solid materials, having relatively high porosity and highly connected pores in which diffusion is predominantly through air, differing from that through still air primarily to the extent that the average cross section of the air path is reduced. In working with textiles, Turl and Kennedy (18) assume that the simple diffusion theory applies and use a method of test which gives a

measure of permeability in terms of an equivalent thickness of still air. In such materials in practice air flow carrying water vapor can also occur as an added mechanism. In addition, convection due to density differences whether due to temperature or to differences in water vapor content can occur. An illustration: diffusion upward through air can be markedly different from that in a downward direction.

Materials in the second category are those which generally have the capacity to sorb water and are of such a nature that this sorbed water enters into the migration process substantially. There is ample reason to suppose that the migration process is now one of a complex series—parallel flow by vapor diffusion in pores, liquid flow in small capillaries which are filled at the particular RH existing, and film flow on other surfaces of greater curvature. The gradient in vapor pressure producing flow leads also to a gradient in RH and thus in the sorbed water, since sorption is primarily related to RH.

Flow under these conditions may involve evaporation and condensation in capillaries or pores. Some thought will show that it can then no longer be strictly isothermal even when equal temperatures are maintained on bounding faces, since evaporation and condensation even on a microscale must involve energy exchanges as well; although it must be questioned whether these will always be represented exactly by the latent heat of evaporation. There is no reason with such a system to expect the simple diffusion concept to apply, and indeed it does not, as evidenced by the functional nature of the apparent permeability coefficient illustrated in a general way by Fig. 5.

It must not be supposed that all materials fall cleanly into one of the three categories described. Obviously there are

many possible combinations, depending on the affinity of the surfaces presented for sorption of water, the pore sizes, and the pore-size distributions, as already discussed. The essential geometry of these systems can seldom be measured directly but is characterized in part by their sorption isotherms as mentioned, and by their moisture transmission properties.

The shape of the permeability curve of Fig. 5 for a particular material must inevitably be strongly related to the nature of its pore structure and surface energy properties. Such curves can be obtained from a series of dish tests carried out at various ranges of RH, each permeance or permeability value obtained being the average value over the particular range for which it was obtained (19).

Unfortunately few such curves are available since they are time consuming to obtain, even when restricted to one temperature. Further work can produce a series of such curves for different temperatures, indicating further the effects of temperature, but these are still not applicable except on a crude approximation basis to the general case, in which both vapor pressure and temperature gradients are imposed.

COMBINED DIFFUSION AND CAPILLARY FLOW

Some workers, notably Krischer, recognized as early as 1940 the essential nature of the moisture migration mechanisms outlined. An extensive bibliography covering European work is contained in a more recent paper by Krischer et al (20). Krischer proposes an equation of the form $G = G_K + G_D$ in which G_K represents the contribution of capillary movement and G_D , vapor diffusion. Johansson (21) proposed a similar equation which for present purposes may be expressed

$$w = -\mu \frac{dp}{dx} - \mu' \frac{dc}{dx} \dots \dots (6)$$

The second part, added to that given as Eq 3, shows a contributory mechanism dependent upon a concentration gradient, or moisture content gradient, dc/dx , and another coefficient μ' . It may now be supposed that the permeability curve of

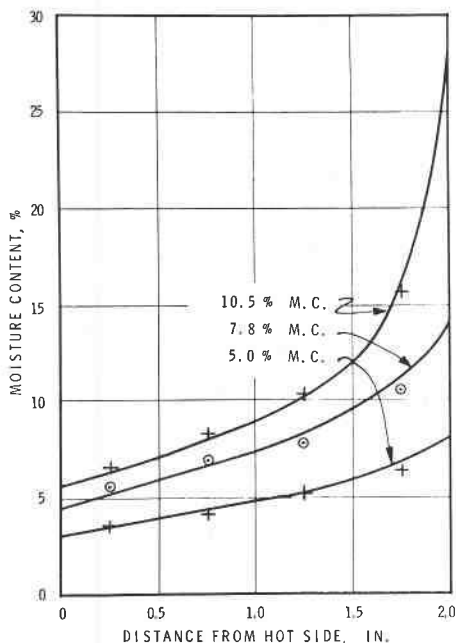


FIG. 6—Comparison of Predicted and Measured Moisture Distributions in Moist Sawdust Subjected to a Temperature Gradient.

Fig. 5 represents a base portion having the characteristics of diffusion, and that the increase with increasing humidity may be attributed to moisture content. Under a nominal isothermal flow condition, both vapor pressure and moisture content gradients will be negative in the direction of flow, so that, according to Eq 6, both contribute to the moisture migration, accounting for the increase in permeability at higher RH.

Some interesting experimental evi-

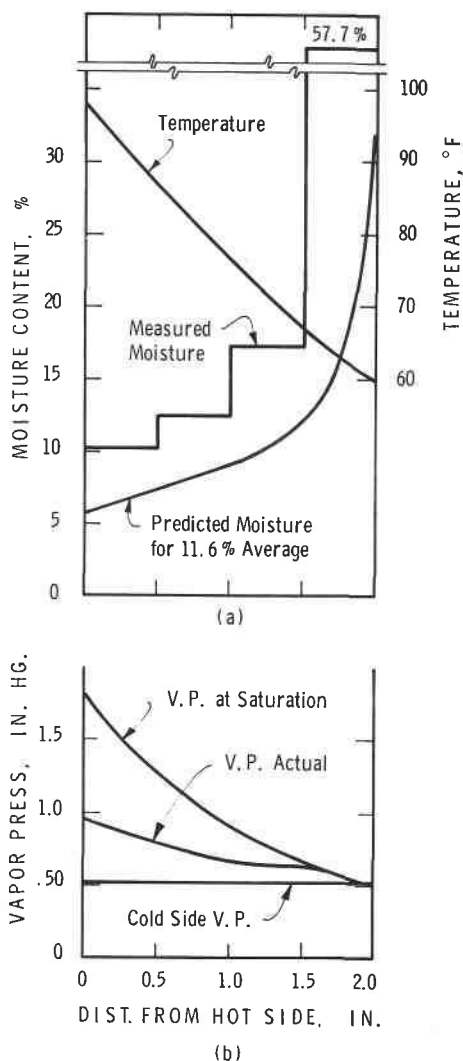


FIG. 7—Final Conditions Throughout a Closed Cell Containing Moist Sawdust Subjected to a Temperature Gradient.

dence is provided by the work of Paxton and Hutcheon (22). The material used was moist sawdust, subjected to a temperature gradient in a closed system so that the net flow across each transverse plane was zero. It was found that the steady-state distributions of moisture could be predicted from the equilibrium

moisture isotherms for wood, on the assumption of a constant vapor pressure throughout, so long as the amount of moisture present was not greatly in excess of that required to produce saturation at the cold face (Fig. 6). When the moisture content was markedly increased, however, the excess moisture did not remain at the cold face, but at all points produced moisture contents higher than those consistent with a constant vapor pressure equivalent to saturation at the cold face (Fig. 7). A curve of actual vapor pressure was then drawn for the values of moisture content actually measured for the four sampling zones (Fig. 7b using equilibrium moisture isotherm data as before) and a vapor pressure gradient was shown to exist.

Further consideration of any such closed system forces one to the conclusion that no net flow takes place. If the equation combines two mechanisms (Eq 6) the contribution of one part must exactly oppose the other at all points along the flow path. Then, if there is a moisture content gradient which can produce flow there must also be an opposing vapor pressure gradient.

At this stage it can be recognized without further argument, that, for a given imposed vapor pressure gradient, the temperature gradient may be varied almost independently, giving rise to corresponding variations in RH and thus in equilibrium moisture content at various points along a flow path. There is thus every reason to believe that a whole stream of values for the permeability coefficient of Eq 3 may be found, depending on the particular combinations of temperature gradients with any given vapor gradient. If this is so, one must accept some such form of flow equation as Eq 6, with its attendant difficulties in relating dc/dx to dp/dx and RH. Thus, both heat flow and moisture flow become involved.

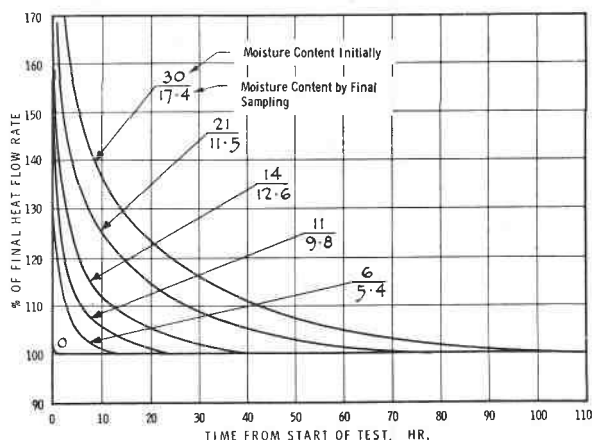


FIG. 8—Variation in Heat Flow with Time in Moist Sawdust Subjected to a Sudden Change in Temperature on One Face.

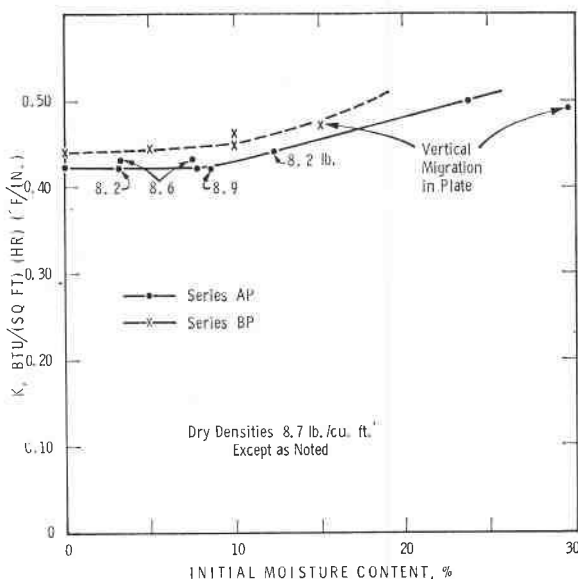


FIG. 9—Variation in Measured Conductivity Under Steady-State Conditions for Various Moisture Contents in Moist Sawdust.

COMBINED HEAT AND MOISTURE FLOW

The difficulty involved in the lack of any adequate mathematical expression to describe moisture migration is far more serious than any of the problems men-

tioned. Not only is there a serious limit on the prediction of moisture migration, but the corresponding capability to predict heat flow in moist materials is similarly restricted. The two flow mechanisms of heat and moisture are so

thoroughly interrelated, one must be considered with the other; it is always appropriate to think of them together as combined heat and moisture flow.

It has long been recognized that the effect of moisture under a temperature gradient is generally to increase the rate of heat flow compared to that in dry material under the same temperature gradient. It is unwise to assume, however, that new conductivities corresponding to various moisture contents can be assigned for use in conduction theory, except in the case of a completely saturated material, since the added energy transfer may be largely associated with vapor flow rather than with a particular level of moisture content. An example of this may be drawn from work previously described (22), as in Figs. 8 and 9. Figure 8 shows the rate of heat flow in moist sawdust at various times after an abrupt change in temperature from a condition of uniform moisture and temperature at 60 deg throughout, to 100 F on one face. These flow rates for the various moisture contents are expressed as percentages of the final steady-state rate. The final rates are shown in Fig. 9 where we see that once moisture redistribution took place, the resulting thermal conductivity was not affected until the average moisture content was increased about $7\frac{1}{2}$ per cent. Beyond that point an increase of about 1 per cent for each per cent increase in moisture content (dry basis) took place. These results are interesting in comparison with those of Cammerer (23), who many years ago proposed two sets of wet conductivities, one for organic and one for inorganic materials. For the former he proposed a value of $1\frac{1}{4}$ per cent for 1 per cent increase in moisture on a dry weight basis and for the latter, a series of values based on moisture content by volume. That is, 1 per cent by volume = 0.625 lb/ft³, as follows:

Moisture Content, %	Increase in Conductivity, %
1	32
2	48
5	75
10	108
20	144

Cammerer's values were developed largely from the experimental work of others. These, or similar values, have been widely used in Europe for want of a more rational method of calculating heat losses through damp building constructions. Clearly, they relate to some arbitrarily selected moisture gradient conditions and cannot rationally account for other gradient conditions which might exist.

MOISTURE MIGRATION IN VARIOUS FIELDS

This discussion has referred to work selected to illustrate the nature of the mechanisms involved. Workers in a number of fields have been concerned with moisture migration, and we will review briefly.

The work of soil scientists concerned with the moisture available to growing crops has been very extensive and outstanding. Being mainly concerned with relatively high levels of moisture content, they have generally worked with the suction concept and have used the negative hydraulic head as the measure of moisture potential rather than vapor pressure. This has several advantages, one being that differences in potential head due to elevation can be taken into account readily. The corresponding permeability coefficients differ from those of the simple vapor diffusion equation by the relationship between RH (or vapor pressure at constant temperature) and negative hydraulic head, or suction. Temperature gradients were not usually accounted for in earlier work. Discus-

sions can be found in any good text on soil physics. Croney et al (24) used similar approaches in predicting the migration of moisture in soils under roads. Philip (25), concerned with agricultural applications, has done extensive work on moisture migration in soils and has taken up the combined heat and moisture flow problem. Taylor (26) has also been concerned with the general case.

Chemical engineers concerned with industrial drying processes have been involved with moisture migration, and another paper in this book reviews developments in this field.

In buildings work, there has been great interest, particularly in Europe, in the effects of moisture upon heat transmission through masonry building constructions. The work of Krischer, Cammerer, and others has already been referred to. In North American building, the interest in theories of moisture migration has developed very little beyond the use of membranes to control vapor diffusion in structures (16). Some work has been car-

ried out on the effect of moisture on heat transmission, but no generally acceptable basis has been established for the estimation of moisture effects.

CONCLUSION

The fire scientist is hampered, as are others concerned with problems of drying, prediction of moisture transfer, and heat transfer in moist materials, by the present limitations in knowledge of combined heat and moisture flow. He has drying problems in the conditioning of his specimens. He is presented, under fire exposure conditions, with high temperature, high gradient, highly transient situations inevitably involving both heat and moisture, which he cannot ignore. He can only hope that at the exaggerated conditions involved in fire exposures, some approximations may be possible which will allow him to predict—with acceptable accuracy for limited purposes—the moisture effects with which he is concerned.

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DISCUSSION

M. S. ABRAMS¹ AND C. C. CARLSON¹—Perhaps concrete ranks with the most complex of building materials because its behavior regarding moisture migration is affected by so many variables. As is well known, the water-cement ratio and the duration of moist curing affect the permeability of the hardened paste. Aggregate type and aggregate pore structure also have important influences on the retention of moisture in, and rate of moisture movement through, sections. We have found that in natural drying for the fire test (drying at normal temperatures and humidities) of concretes containing expanded shale aggregates, the required drying time may be twice that for concretes containing natural sand and gravel aggregates, even though the cement content and initial moist curing are identical. On the other hand, some lightweight aggregate types such as those produced by a sintering or quenching process may produce concretes that will lose water more rapidly than some normal weight concretes by virtue of the coarser and interconnected pore structure of the aggregate particles.

Perhaps the most interesting fact of regarding the movement of moisture through concrete is that it moves primarily in a condensed state rather than in the vapor phase. Under such conditions the driving force that moves the moisture is not proportional to the vapor pressure differential between the at-

mosphere and the concrete, but to the logarithm of the ratio of these pressures. Thus, for concrete at a given equilibrium vapor pressure, a pressure of many atmospheres is required to produce a given moving force when the water migrates in the adsorbed or condensed state. Large driving forces are obviously not generated under normal drying conditions so the migration of moisture in mature concrete is therefore often a slow process.

We agree with the authors that RH does not uniquely define the moisture content of concrete. RH is useful in evaluating the heat transmission properties of concrete which has been naturally conditioned for the fire test. However, it has, as we have found, some serious drawbacks as an indicator of fire endurance when drying is accelerated by heated air.

P. J. SEREDA AND N. B. HUTCHEON (*authors*)—We agree that migration of moisture in concrete is a slow process and in this regard we will amplify the above remarks. When a vapor pressure gradient exists it will result in vapor diffusion as well as flow of moisture in the condensed state. For the vapor diffusion process the rate can be expressed as the product of the coefficient μ and the vapor pressure difference; the coefficient usually being a function of the moisture and temperature conditions as well as of the material. Because the capillaries in concrete are very small much of the flow of moisture can occur in the condensed state and may be represented by the product of an appropriate coefficient

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and the suction gradient. The suction gradient is the gradient in the negative head, which can be very large for small gradients of vapor pressure; the potential difference between two sections of concrete, one at equilibrium with 50 per cent RH and another at equilibrium with 99.99 per cent RH will be 10^4 cm of water. The rate of flow of water resulting from such a high potential difference, however, is relatively small because the corresponding permeability coefficient is small.

D. HANSEN²—Equation 3 is labeled "a form of Fick's law." This is not absolutely true. While Fick's law of diffu-

sion, under special conditions, may be put in the form of Eq 3, neither these conditions, nor the law itself, applies to the present situation of diffusion in a porous medium. However, Eq 3 is commonly used for describing diffusion in porous media, and I have no objection to its application in this case.

MR. SEREDA AND MR. HUTCHEON—We do not wish to dispute the point made by Professor Hansen. In referring to a form of Fick's law we were following the lead of J. D. Babbitt, who did much to establish the diffusion approach to the migration of moisture through building materials.³

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³ "The Diffusion of Water Vapour Through Various Building Materials," *Canadian Journal of Research*, Vol. 17, Section A, 1939, pp. 15-32.

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