THE MOISTURE POTENTIAL

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The theory of non-steady state moisture transfer under nonisothermal conditions, as applied to structures, is developed in terms of the moisture potential.

Moisture transfer in building structures is usually caused by a difference in moisture content, pressure, temperature and forces due to variation in the binding energy of water in materials that are in contact with each other.

In 1952 the author proposed and developed a method of calculating moisture transport in structures based on the "moisture potentials," which is a "total potential" in the thermodynamic sense. When defined on a suitable scale, it can be used to calculate all the force factors acting upon moisture. Movement of moisture, in both the vapor and the liquid phase, is determined by the moisture potential gradient, and the accumulation of moisture by the moisture capacity, expressed in terms of change in moisture potential.

The physico-mathematical basis of the moisture potential method has been given in [1, 2], where stress is laid on the intimate connection between the phenomena of heat and mass transfer, which are described by the methods of the thermodynamics of irreversible processes.

The physico-mathematical formulation, based on the moisture potential, is of prime importance for the analysis of moisture transport processes in structures. This formulation permits the examination of moisture transport processes in multi-layer structures over a wide range of moisture contents and temperatures and the calculation of moisture migration in the vapor and liquid states under the action of various forces, among them the temperature gradient.

Moist material can be regarded as an open heterogeneous system comprised of two parts or components. One part, the skeleton of the material, is an invariant component. The second component of the system is the absorbed substance, water, the amount of which may vary.

Changes in the internal energy of a small element of volume of the moist substance dE are given by the Gibbs equation

$$dE = VdP - SdT + \Sigma \Theta \, dm. \tag{1}$$

The terms V, dP, S, dT relate to the skeleton of the material. Changes in energy are determined by variation in the absorbed moisture (its amount and state) and are given by the last term in the equation.

Moisture transport in building materials is a very slow process; therefore water vapor in the moist air penetrating the pores and capillaries of the material must be in molecular and thermodynamic equilibrium with liquid at every point. The moisture capacity of the small amount of moist air in the pores of the material is so low that an insignificant change in the state of the liquid moisture absorbed in the pores produces an almost instantaneous readjustment in the equilibrium between the liquid and vapor phase in every pore. The same applies to the liquid phase when the state of the moist air in the pores varies. The temperature at any point will be the same in liquid moisture, moist air, and solid skeleton. Under conditions of thermodynamic equilibrium the vapor and liquid phases of the moisture have the same potential. Therefore the moisture potential will be equal for moisture phases of different state.

The moisture potential is the total potential of the moisture. It is defined by the potential of all force fields acting on the moisture.

The force field caused by variation of the moisture content in different parts of the solid determines the potential Θ_i , which is analogous to the so-called capillary potential. Fundamentally, the potential Θ_i depends on the surface tension of the liquid and the radius of curvature of its surface. With increase in the quantity of liquid moisture in the material the pores and large capillaries fill up. The mean radius of curvature of the liquid surface is thus increased, which in turn increases the value of the potential. The temperature affects the surface tension and the potential Θ_i . Thus, the potential Θ_i is basically determined by the moisture content, the temperature, and the nature of the material.

The gravitational force field acting on the liquid determines the potential Θ_g , the magnitude of which depends only on the vertical distance from an arbitrary reference level. The potential Θ_g is a maximum at the level of a free liquid water surface in contact with the moist solid. The potential Θ_g decreases with distance from the free liquid surface, tending to zero at an infinite distance. The potential Θ_g does not depend on the moisture content, the temperature, or the nature of the material. The force field that allows for the salinity of the water, the osmotic pressure, etc., can be considered separately and defined by the potential Θ_T , which depends, together with other factors, on the moisture content, the temperature, and the nature of the material.

The moisture potential is a total potential, since it is determined by the moisture content, the temperature, the nature of the material, and the distance measured above a free water surface. All of the potentials examined have the same dimension and the same energy interpretatation – the specific energy referred to mass of moisture.

A discussion of potential, based on the application of thermodynamic methods, is governed by two laws.

According to the first law, under conditions of thermodynamic equilibrium, the potentials of the solid must be the same at every point. Applied to our case, this means that when there is moisture equilibrium in the material or system consisting of several materials, i.e., when the moisture conditions at individual points of the solid are time-invariant, the moisture potential Θ will be equal at all points. This conclusion is correct when any one force field acts on the solid, and when several of the above-mentioned force fields act on the solid simultaneously.

This law can conveniently be employed in the construction of a moisture potential scale.

The moisture potential can be determined with the aid of a scale of gravitational potential, which, as follows from the above explanation, is a geometric scale of height above a free water surface. Use of this scale makes it possible to compare the action of other force fields with the action of the gravitational field. As pointed out, this scale is convenient in that it does not depend on the temperature, the nature of the material, or on other factors affecting the moisture. However, this scale has a fatal drawback, a small amount of moisture corresponds to a very large distance from the free water surface. Therefore, in order to employ this scale, one would have to prepare a very tall column of material. Furthermore, the conditioning of this column for the measurement of the potential of a small amount of moisture would require a very long time.

A simpler measurement of the moisture potential can be made employing the potential scale Θ_i . The potential Θ_i depends on several factors but primarily on the moisture content, temperature, and the nature of the material. Therefore in conducting these measurements it is necessary to exclude the influence of other factors on the potential scale and leave only one – the moisture content of the material. To do this it is convenient to adopt as a potential scale the change in moisture content of a definite (standard) material at a constant (standard) temperature, and thus eliminate the influence of temperature and the nature of the material on the scale.

The moisture potential of any moist material can be determined by employing as a comparison scale the change in equilibrium moisture content of a standard material at a standard temperature.

For application to moisture transport through the walls of structures it is most important to know the value of the moisture potential of various materials under different moisture and temperature conditions.

The moisture potential of various materials under different moisture and temperature conditions is determined on a single equilibrium moisture scale for a standard material at standard temperature under equilibrium conditions, i.e., when the materials are placed in contact so as to permit free (completely unrestricted) moisture exchange until total moisture equilibrium is attained.

To obtain the temperature dependence of the moisture potential of materials it is necessary to carry out experiments in which moisture equilibrium is attained under different temperature gradients. In this case it is possible to compare equilibrium moisture contents at arbitrary temperatures with equilibrium moisture contents at the standard temperature, i.e., to fix them on a single moisture potential scale.

The proposed method for the construction of a moisture potential scale allows the temperature dependence of the moisture content of a material to be related to the moisture potential by means of simple experiments. First, we used sand as a standard material, and later, sawdust and other materials. We decided that the most convenient standard material for the construction of a moisture potential scale was filter paper at room temperature $+20^{\circ}$ C, the moisture potential being measured in degrees of moisture content, $^{\circ}$ M. The scale is assumed to be uniform. Zero moisture content of the standard material corresponds to the zero of the moisture potential scale -0° M. The point 100° M on the scale corresponds to a moisture content of the standard close to the so-called maximum hygroscopic moisture content.

The maximum hygroscopic moisture content of the material corresponds to moisture equilibrium with air fully saturated with water vapor.

However, experiments showed that lengthy exposure to air fully saturated with water vapor causes pores and capillaries with a nominal radius of 10^{-5} cm to fill. This corresponds to air with a relative humidity of 99%. Therefore we may assume that the maximum hygroscopic moisture content of the material corresponds to the same figure. In this case 100% saturation of the air can be taken as corresponding to the total saturation moisture content of the material. However, under the experimental conditions, such a state is practically impossible to attain. The moisture capacity of the material depends, as a rule, on the moisture potential and the temperature. At a given temperature the true moisture capacity is

$$\eta = \frac{dU}{d\Theta} \ . \tag{2}$$

(3)

The second law governing the potential is that transport of energy (mass) occurs in the direction from high to low potential.

By analogy with other physical phenomena it is assumed that the moisture flux in the material i is proportional to the gradient of the moisture potential $\nabla \Theta$

$$i = H \nabla \Theta.$$

The simplest and best experiment to construct a curve of the moisture content of the material vs. the moisture potential and to determine the coefficients of moisture capacity and moisture conduction is the "sectional-column" method. This method has several advantages.

The chief feature of this method is that, thanks to the use of packets of filter paper, which might be called "moisture meters," it gives a direct determination of the moisture potential at several levels of a test specimen under conditions of constant moisture flux. The values of the moisture potential (under isothermal conditions at T_{st} the potential is equal to the moisture content of the packets of filter paper) is correlated with the moisture content of the layers of material in the column; thus it is possible to carry out the experiment in various regions of moisture potential, and knowing the moisture flux, to obtain all the required relations; a) between the moisture content of the material at various temperatures and the moisture potential $U = f(\Theta;T)$; b) between the coefficient of moisture capacity and the moisture potential at different temperatures $\eta = f(\Theta;T)$; c) between the moisture conductivity and the moisture potential and temperature H = $f(\Theta;T)$.



Fig. 1. Dependence of U (1), η (2), and H (3) at the standard temperature and U_{u.w.} at negative temperatures (4, 5, 6) on Θ .

These relations are shown in Fig. 1. The curves 1, 2, 3 are constructed from laboratory data obtained by the "sectional column" method. The relation $\eta = f(\Theta)$ was obtained by graphical differentiation of the data. The relation $H = f(\Theta)$ was obtained by direct analysis of the results of the "sectional column" experiments.

The general mathematical expression for non-steady state moisture transport in the interior of a material is the differential equation of the moisture potential field, which, taking into account the usual nonlinearity of the coefficients, for a one-dimensional field has the form:

$$\eta(\Theta; \mathbf{T}) \gamma_0 \frac{\partial \Theta}{\partial \tau} = \frac{\partial}{\partial x} \left[\mathbf{H}(\Theta; \mathbf{T}) \frac{\partial \Theta}{\partial x} \right].$$
(4)

To obtain the non-steady state moisture field $U(x;\tau)$ it is necessary to recompute values of $\Theta(x;\tau)$ using the relation $U = f(\Theta;T)$.

In examining moisture transfer at the surface of a structure we are usually concerned with moisture exchange between the structure and the surrounding moist air. In order to fix the surface conditions, we need to express the state of the moist air at various temperatures with the aid of the moisture potential scale. This relationship can be obtained experimentally, on the basis of the first law relating to the potential, which we examined in connection with the construction of a moisture potential scale. Knowing the sorption-desorp-

tion isotherm of any material in moist air at various temperatures, and also the dependence of the moisture content of this material on the moisture potential in the hygroscopic region at the same temperatures, by a simple construction it is possible to obtain the relation between the relative moisture content ϕ_a and temperature T_a of the air and its moisture potential Θ_a . This relation fully determines the moisture potential of the air whatever its hydrothermal state, independently of the properties of the material whose data are employed in this construction.

Figure 2 gives the sequence of constructing $\Theta_a = f(T_a; \phi_a)$ using the sorption isotherms and the isothermal dependence of the equilibrium moisture content of the filter paper $U_{f,p}$, on the moisture potential.



Fig. 2. Plot of a) $\Theta = f_a(\phi_a;T_a)$ from the data b) $U_{f.p.} = f(\phi, T)$ and curves c) for the moisture potential $U_{f.p.} = f\Theta$, T): $1 - T = 10^{\circ}C$; 2 - 20; 3 - 30.

Moisture in frozen materials. All the conclusions about the moisture potential remain true for the negative temperature region, where part of the moisture is converted to ice, and between the water phases there are established the quantitative relations characteristic of the law of phase equilibrium in frozen materials. The basic premise of this law is that in frozen material of a definite form a certain negative temperature corresponds to a definite quantity of unfrozen, liquid water. The latter does not depend on the total quantity of moisture in the material, if the latter is larger than the quantity of unfrozen moisture determined for a given temperature. The method of moisture potential enables us to express, in degrees of moisture, the state of the unfrozen moisture, its mobility H, and the moisture capacity of the material in the negative temperature region. To do this, it is sufficient to extend to this region the experiments for determining the above properties, using the methods described.

The approximate characteristics of these relations can be obtained by applying the known parallel between freezing and drying phenomena. If we ignore the temperature dependence and the influence of ice crystals in the pores and capillaries of the frozen solid, we can assume the characteristics $U = f(\Theta; T)$, η and H to be the same for frozen as for unfrozen materials with a moisture content equal to the amount of unfrozen moisture. These calculations may be performed more accurately if the temperature dependences of the corresponding characteristics are extrapolated into the region of negative temperatures.

Figure 1 presents data obtained from laboratory experiments on the content of unfrozen water $U_{u.w.}$ (4) in red brick at various negative temperatures (T). By way of example, the amount of unfrozen moisture in red brick $U_{u.w.}$ has been plotted against the moisture potential (Θ) at T = -2° (5) and -8° C (6) using the same data.

It is interesting to note that the known dependence of unfrozen moisture on the pressure on frozen earth can be thermodynamically explained in terms of moisture potential by analogy, for example, with the effect on moisture of a gravitational force field. Pressure is one of the components of the total potential corresponding to the moisture potential; therefore changes in pressure under conditions of thermodynamic equilibrium, when the other force fields are maintained constant, must produce changes in the moisture potential, and hence in the quantity of unfrozen water.

To analyze the moisture behavior of structures we need to know the temperature field, and to obtain this we must solve the corresponding differential equation of the field with boundary conditions and other conditions of uniqueness.

As already pointed out, a feature of processes in structures is the comparative rapidity of heat transfer processes and the slow development of moisture fields. In view of this, it is possible first to calculate the temperature field, taking into account the assumed indirect influence of moisture transport: the moisture content of the materials – in choosing the thermal conductivity and heat capacity, and the moisture transfer – in choosing the heat transfer coefficients at the surfaces. Knowing the temperature field, it is possible to calculate the moisture potential field and convert it to the moisture content field. A feature of the calculation of the moisture content field is the significant dependence of the coefficients H and η on Θ and T, which it is almost impossible to take into account by averaging, and also the presence of complex dependences of Θ on U and T and of the moisture potential of the air Θ_a on ϕ_a and T_a . To solve this problem analytically it is necessary to divide the space-time continuum into numerous zones within which the chief characteristics of the process are invariant in space and time. Given a large number of zones, the analytical method approaches the method of finite differences, which therefore is also suitable for solving the problem. However, the most successful method is by analogy using an analog computer, for example, an hydraulic integrator. For some time, similar problems have also been solved on electronic computers.

NOMENCLATURE

V - volume; dP - pressure increment; S - entropy; dT - temperature increment; Θ - total potential of moisture in material; m - mass of moisture; H - proportionality factor, moisture conductivity; γ_0 - weight per unit volume of completely dry material.

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