France-Japan Workshop on Mass-Energy Transfer and Deterioration of Building Materials and Components,
22-23 January 1998, Tsukuba, Japan

An Overview of Principles and Techniques of Moisture Properties Measurement for Building Materials and Components

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1. Introduction

2. Water transport and related moisture properties
2-1 Basic water transport equations
2-2 Physical meaning of the moisture properties

3. Moisture content
3-1 Nuclear Method
    (1) Gamma-ray attenuation
    (2) Nuclear magnetic resonance
    (3) Neutron attenuation
3-2 Thermal conductivity method
    (1) Principle of measurement
    (2) Application
3-3 Electric method
    (1) Direct current resistance
    (2) Capacitance
    (3) Various electromagnetic waves
3-4 Ultrasonic method
    (1) Principle of measurement
    (2) Application

4 Sorption isotherm
    (1) Saturated salt solutions
    (2) Changing temperature or pressure
    (3) Flow division
    (4) Changing vapor pressure in vacuum
    (5) Transient method

5. Moisture characteristics
5-1 Pressure plate
5-2 Psychrometric method
5-3 Tada method
    (1) Water vapor adsorption
    (2) Mercury injection

6 Water vapor diffusivity
6-1 Cup method
6-3 Sorptivity method
    (1) Principle of measurement
    (2) Application

7 Water conductivity
7-1 Moisture profile methods
7-2 Bolzmann transformation method
7-3 Moment method
7-4 CSTB method

8 Conclusions

1. Introduction

Major building materials such as wood and concrete are porous and their time-dependent behaviors are widely dominated by moisture transfer. Quantitative treatments of the moisture transport by simulating the variation of moisture conditions in materials have been an important task, where the measurement of the moisture properties is the rate-determining process and rapid measuring techniques have been required.

We have presented an overview of principles and techniques of measuring moisture related properties of construction materials anticipating the development of more efficient and rapid methods. Although flows of energy and other masses coupled with water flow and respective cross coefficients are of great importance, isothermal water transfer is only dealt with in this paper.

2. Water transport and related moisture properties

2.1 Basic water transport equations

The significance of moisture transfer properties that appear as coefficients in the set of basic equations is first examined according to Daïan(1). The moisture balance equation with moisture content θ in kg/m^3 as an apparent driving force at an isothermal condition can be expressed as

$$\nabla \cdot \mathbf{J} + \frac{\partial \theta}{\partial t} = 0, \tag{1}$$

where ∇ is the Hamilton's operator, nabla, and the mass flux $\mathbf{J}$ can be regarded as a sum of a vapor flux $\mathbf{J}_V$ and of a liquid flux $\mathbf{J}_L$.

Without total pressure difference and hence without convective vapor flow, the vapor flux in a porous material follows Fick's law

$$\mathbf{J}_V = -D_V \nabla p_V, \tag{2}$$

where D_V is the vapor conductivity and p_V is the vapor pressure (Pa). Relative pressure h can be preferably chosen as an alternative driving force, so that the vapor flux can be expressed as

$$\mathbf{J}_V = -p_{VS} D_V \nabla h, \tag{3}$$

where p_{VS} is the saturated vapor pressure at the temperature. The liquid flow may be described in terms of the unsaturated Darcy's flow. When the gravitational effect can be negligible

$$\mathbf{J}_L = -\frac{K}{\mu} \nabla p_C, \tag{4}$$

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(1) Daïan, J-F., Condensation and isothermal water transfer in cement mortar, Transport in Porous Media, 3, 563-589, 1988

where K is the specific permeability, μ is the dynamic viscosity of liquid water and p_C is the capillary pressure. With $P_c = RT(\ln h)/v$, we have

$$\nabla p_C = \frac{RT}{vh}\nabla h, \tag{5}$$

where R is the gas constant, is the temperature and is the specific volume of water. Both vapor flow and liquid flow can be expressed in terms of relative pressure gradient,

$$\mathbf{J}_V = -D_{hV}\nabla h, \quad \mathbf{J}_L = -D_{hL}\nabla h, \tag{6}$$

with

$$D_{hV} = \rho_{VS} D_V, \quad D_{hL} = \frac{K_L}{\mu}\frac{RT}{vh}. \tag{7}$$

Because the relative pressure h can be a common driving force for vapor and liquid flows, it has been widely used as a driving force of moisture flow in concrete(2).

For conveniences of measurement, moisture content gradient $\nabla\theta$ is preferably chosen as a driving force. We have,

$$\nabla h = \frac{\partial h}{\partial \theta}\nabla\theta, \ \nabla p_C = \frac{\partial p_C}{\partial \theta}\nabla\theta. \tag{8}$$

The respective moisture fluxes can now be expressed in terms of moisture content gradient,

$$\mathbf{J}_V = -D_{\theta V}\nabla\theta, \quad \mathbf{J}_L = -D_{\theta L}\nabla\theta, \tag{9}$$

where,

$$D_{\theta V} = \rho_{VS}\frac{\partial h}{\partial \theta}D_V, \quad D_{\theta L} = \frac{K_L}{\mu}\frac{\partial p_c}{\partial \theta}. \tag{10}$$

With $D_\theta = D_{\theta V} + D_{\theta L}$, we have the global moisture flux as

$$\mathbf{J} = \mathbf{J}_V + \mathbf{J}_L = -D_\theta \nabla\theta, \tag{11}$$

so that the moisture balance equation can be expressed in terms of moisture content gradient

$$\nabla(D_\theta \nabla\theta) = \frac{\partial\theta}{\partial t}. \tag{12}$$

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(2) Bazant, Z. P. , Najjar, L. J., Nonlinear water diffusion in nonsaturate concrete, Materials and Constructions, 5(25) 3-20, 1972

2.2 Physical meaning of the moisture properties

The moisture transfer properties of concern are θ, $\partial h/\partial\theta$, $\partial p_C/\partial\theta$, $D_{\theta V}$ and $D_{\theta L}$ that have to be determined by experiments. The $\partial h/\partial\theta$ is the inverse number of the moisture capacity that is defined as an increment of moisture content with a change in relative humidity, and can be obtained as a gradient of sorption isotherm.

The $\partial p_C/\partial\theta$ is an increment of capillary pressure with a change in relative humidity, and can be obtained as a gradient of the moisture retension curve.

The $D_{\theta V}$ and $D_{\theta L}$ are the vapor diffusivity and the water conductivity to be obtained as a function of moisture content.

We will call these values as moisture properties and their determination techniques will be discussed in the following section. However, permeability which is a conductivity of saturated media under total pressure difference will be excluded because the measurement techniques have been well documented in the literatures(3)(4).

3. Moisture content

Measurement of moisture in materials has been required from wide variety of industries as an indispensable process control technique. In 1963, an international symposium on humidity and moisture was held, where 36 papers dealing with measurement of moisture in solid were presented(5). In the second symposium organized in 1985, 13 papers on moisture in liquid and solid were presented(6) including a review paper by Maley(7).

Measuring techniques of moisture content applicable to building materials have been preceded by the soil science(8), and Wormald and Britch(9) discussed the portability to building materials. Whiting(10) reviewed wide range of techniques applicable to in-situ, non destructive testing.

3-1 Nuclear Method

(1) Gamma-ray attenuation

The transmission of a collimated beam of monochromatic gamma rays through dry materials can be described by the following attenuation equation,

$$\ln(I/I_0) = -\mu\rho d\,, \tag{14}$$

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(3) Conference. on Permeability of Concrete and its control, 12, September, 1985, London

(4) Geiker, M., Grube,. H., Luping, T., Nilsson, L-S. and Andrade, C., Laboratory test methods, in Kropp, J. and Hilsdorf, H. K. eds "Performance Criteria for COncrete Durability, 213-257, E & FN SPON, 1995

(5) Int. Symp. Humidity and Moisture, vol.4, Principles and methods of measuring moisture in liquid and solid,20-23, May, 1963, Washington DC.

(6) Int. Symp. Moisture and Humidity、 15-18, April, 1985, Washington DC.

(7) Marley, L. E., Continuous moisture analysis instrumentation, 649-657 in ref.(6), 1985

(8) Yabe, K., Soil moisture measurement, SPCPG, (41), 90-94, 1980 (in Japanese)

(9) Wormald, R., Britch, A. L., Method of measuring moisture content applicable to building materials, Build. Sci., 3, pp.135-145, 1969.

(10) Whiting, D., Assessment of poential techniques for in-situ, real time moisture measurement in building envelope systems - A literature survey, DOE report, W-7405-eng-26, 85 p 1983

where I (counts/s) is the intensity of transmitted beam, I_0 is the intensity of incident beam (counts/s), μ is the mass absorption coefficient (m^2/kg), ρ is the bulk density of the specimen and d is the thickness of the specimen.

Similarly, the attenuation of a collimated beam through wet materials is described by,

$$\ln(I/I_0) = -d\left(\mu_s\rho_s + \mu_w\rho_w\right), \tag{15}$$

where subscripts s and w denote specimen and water. The moisture content φ (m^3/m^3) can be expressed as,

$$\varphi = \frac{\ln\left(I_s/I_w\right)}{\mu_w\rho_w d}, \tag{16}$$

where I is the intensity of the dry specimen, I_w is the intensity of wet specimen. The absorbing coefficient and the bulk density must be determined in each materials.

Attempts to use gamma-ray for the determination of moisture content of porous materials started in the 1950s in the soil science(11), and later in the 1970s, Nielsen(12) applied this method to non destructive determination of the moisture content of autoclaved aertaed concretes. Because of difficulties of in-situ measurement, applications made by Daian(13), Quenard and co-workers(14) and Kumaran and co-workers(15) were water conductivity measurement in the laboratory. Recent applications are described in detail by Descamps(16).

(2) Nuclear magnetic resonance

Atoms with different number of proton and neutron, such as hydrogen atom, have dipole moment μ and, when place in the external magnetic field B_o, behave like a gyro in the gravitational field. Frequency of the gyroscopic precession ω_o is proportional to the intensity of the external magnetic field. Taking γ as the material constant, the gyromagnetic ratio,

$$\omega_o = \gamma \cdot B_o. \tag{17}$$

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(11) Ferraz, E. S. B., Gamma-ray attenuation to measure water contents and/or bulk densities of porous materials, Proc. Isotope and Radiation Technology in Soil Physics, 449-460, 1983

(12) Nielsen, A. F., Gamma-ray attenuation used for measuring the moisture content and homogeneity of porous concrete, Building Science, 7, 257-263, 1972

(13) Daïan, J-F., Condensation and isothermal water transfer in cement mortar, Transport in Porous Media, 3, 563-589, 1988

(14) Quenard, D. and Sallee, J., A gamma-ray spectrometer for measurement of the water diffusivity of cementitous meterials, MRS Symp. Proc. Boston, 137, 165-169, 1989

(15) Kumaran, M. K., Mitalis, G. P., Kohonen, R. and Ojanen, T., Moisture Transport Coefficient of Pine from Gamma Ray Absorption Measurements, ASME-HTD 123, 179-183, 1989

(16) Descamps, .P., Continuum and discrete modelling of isothermal water and air in porous media, Thesis, Kathoric University of Leuven, 1997
http://www.bwk.kuleuven.ac.be/bwk/physics/fd01.htm

The energy difference of two quantum levels ΔE depends on the magnitude of the external magnetic field B_o and the magnetic moment of the atomic nucleus.

$$\Delta E = \frac{\gamma \cdot B_o \cdot h}{2\pi} \tag{18}$$

where h is the Planck's constant. When the velocity of the gyroscopic precession coincides with the frequency of radio waves emitted on the specimen, absorption takes place.

To determine the number of proton in the specimen, a constant magnetic field should be applied to the specimen followed by the measurement of energy of the absorbed radio wave. The relationship between the frequency of the radio wave and the absorption coefficient is affected by the duration of excited state of the nucleus (relaxation time). Because the relaxation time depends on the environment in which the proton is placed, the spin-lattice relaxation time T_1 or the spin-spin relaxation time T_2 should be measured. The former is an energy exchange between the proton and the surrounding water molecule structures while the latter is an energy exchange between spins and nothing to do with the surrounding water molecules.

Thus the determination of T_1 and T_2 can give a quantitative information on the degree of binding of water molecules, such as free, physically adsorbed or chemically adsorbed water, in the presence of the solid. The relaxation time corresponds to the induced electromotive forces (FID signal) in the coil.

The nuclear magnetic resonance (NMR) method was first applied to building materials for moisture content determination in the late of the 70s by Matzkanin and co-workers(17). Gummerson and co-workers(18) traced the changes in moisture content in specimens.

In the determination of water diffusivity, it is necessary to measure the changing moisture content in specimens in a non destructive, continuous manner. Pel(19) determined the moisture content distribution of specimens, set vertically to absorb water, by traversing coils. Kissel and co-workers(20) executed similar experiments using a compact apparatus. The specimens were set horizontally, the maximum cross section was 50 x 50 mm, traverse resolution as high as 4 mm and the accuracy of moisture content determination was 0.5 to 1.0 percent by volume. Measurement duration was 3 to 10 minutes when the length of the specimen was 150 mm. The results were reported to be in good agreement with those measured by the gamma-ray attenuation method.

(3) Neutron attenuation

Gamma-rays and X-rays interact with electrons while neutrons interact with the nucleus

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(17) Matzkanin, G. A. and Gardner, C. G., Nuclear magnetic resonance sensors for moisture measurement in roadways, Transport Research Record No. 532, pp. 77-85, 1975

(18) Gummerson, R. J. et al., Unsaturated water flow within porous materials obseved by NMR imaging, Nature, 281, pp.56-57, 1979

(19) Pel, L., Moisture transport in porous building materials, Ph. D. thesis, Eindhoven University of Technology, The Netherland, 1995
http://www.phys.tue.nl/nfcmr/cmrmain.html

(20) Kissel, K. and Krus, M., Experimental Determination of Building Materials Properties for Moisture Calculation, Proc. Int. Workshop on Mass-Ennergy Transfer and Deterioration of Building Components - Models and Characterisation of Transfer Properties, Paris, 322-342, 1995

of the mass, especially with protons, and become thermal neutrons loosing energy by absorption and scattering. Influences of proton is so large that the detected thermal neutrons show a linear correlation with the number of proton per unit volume of the specimen. Unlike NMR method, neutron attenuation method cannot give information on the binding state of water molecules, and has difficulties in apparatus and its management because the beam source is more or less a reactor.

Roethig(21) recommended the neutron attenuation method as the most suitable one for the process moisture control in the factory. A surface contact detector has been developed and widely used but the dimensions of specimens are as large as 20 cmm cube. Pel(22) used neutron beam to scan the specimen for water conductivity measurement. It was reported that the sensitivity to moisture content was 1 % and the spacial resolution was 1 mm. A neutron radiography method(23) was recently in use. It can determine moisture content distribution by analyzing the grayscale images, which corresponds to the density of proton, on the photosensitive films.

3-2 Thermal conductivity method

Moisture in materials affects the thermal conductivity so sensitively and linearly that the rapid measurement of the thermal conductivity can give information on the moisture content without effects of salts. A method applicable to this purpose is the hot-wire method, a transient thermal conductivity measurement technique.

The hot-wire method was first formulated in the 1940s by van der Held and subsequently applied to construction materials by Granholm and Sarre(24) in 1952. Meeting the requirements for the outdoor use in civil and agricultural engineering, Blackwell(25) developed a mathematical theory of probe method. Joy(26) and Vos(27)(28) measured thermal conductivity of a variety of wet materials by the probe method. Indirect measurement of moisture content by the hot-wire method was proposed by Vos.

(1) Principle of measurement

A heater wire extends perpendicular to a thermocouple which is sufficiently thin to receive heat per unit length of the wire as shown in Fig.1. It is further assumed that the

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(21) Roethig, R., Zerstrorungsfreie Prufung von Gasbetonelementen. Eine Untersuchung zum Stand der Technik, Baustoffind. Ausg., 19(2), 16-21, 1976

(22) Pel, L., ibid. Blackerll, J. H., A transient-flow method for determination of thermal constants of insulating materials in bulk, J. Appl. Phys., Feb, 137-144, 1954

(23) Justnes, H., Bryhn-Ingebrigtsen, K. and Rosvold, G. O., Neutron radiography: an excellent method of measuring water penetration and moisture distribution in cementitious materials, Adance in Cement Research, 6(22), 67-72, 1994

(24) Saare, E., Jansson, I., Measurement of thermal conductivity of moist porous building materials, RILEM Int. Conf. Lightweight Concr., Gotegorg, 353-370, 1960

(25) Blackerll, J. H., A transient-flow method for determination of thermal constants of insulating materials in bulk, J. Appl. Phys., Feb, 137-144, 1954

(26) Joy, F. A., Thermal conductivity of insulation containing moisture, Symp ASTM, 65-80, 1957

(27) Vos, B. H., Non-steady-state method for the determination of moisture content in structure, Proc. Int. Symp. Humidity and Moisture, Woshington, Vol. 4, 35-47, 1963

(28) Vos, B. H., Measurement of moisture content in building, Proc. RILEM/CIB Symp. Moisture Ploblem in Building, Helsinki, 1966

surrounding medium, a specimen, is homogeneous and initial condition is anywhere in the specimen when the heater is ON at t=0. The transient heat conduction law is,

$$Cd\frac{\partial\theta}{\partial t}=\lambda\frac{\partial^2\theta}{\partial x^2}. \tag{19}$$

The solution for the coaxial conduction is,

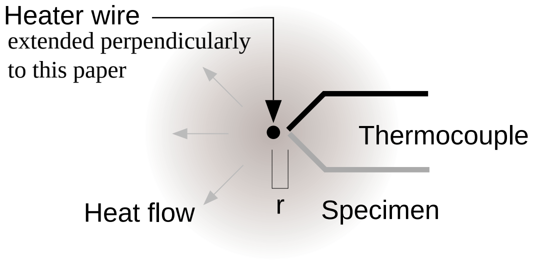

Fig. 1 Arrangement of hot-wire sensor

$$\theta=\frac{q}{4\pi\lambda}\int_0^t\frac{1}{t'}\exp\left(-\frac{r^2}{4at'}\right)dt', \tag{20}$$

where a is thermal diffusivity (m2/s), λ is thermal conductivity (W/mK), q is heat generation per length (W/m), r is the distance from the heater to thermocouple (m), θ is temperature (K) and t is time (s), and the error function term in the integral term is approximated to 1.

Because what is important is not θ but changes in temperature with time, differentiating equation (20) with $\partial\ln t$ to determine $\partial\theta/\partial\ln t$ experimentally gives,

$$\frac{\partial\theta}{\partial\ln t}=\frac{q}{4\pi\lambda}\exp\left(-\frac{r^2}{4at}\right), \tag{21}$$

where $\exp\left(-r^2/4at\right)$ can be reduced to 1 by bringing the thermocouple close to the heater.

The basic equation for the hot-wire method can be given as,

$$\frac{\partial\theta}{\partial\ln t}=\frac{q}{4\pi\lambda}. \tag{22}$$

(2) Application

Expressing equation (22) in terms of λ and electromotive force of the thermocouple, we have

$$\lambda=\frac{q}{4\pi}\cdot\frac{\partial\ln t}{\partial\theta}=\frac{\partial E}{\partial\theta}\cdot\frac{\partial\ln t}{\partial E}\cdot\frac{q}{4\pi} \tag{23}$$

where $\partial E/\partial\theta$ is the electromotive force of a chromel-arumel thermocouple 0.04065 (mV/deg).

As the time of measuring the voltage rise (temperature rise) is controlled by a stopwatch, easy-to-read timing of 30 and 60 seconds after the heater is on were selected, when $\partial\ln t$ becomes $\ln 2$. With the unit resistance of the heater wire of 6.217 (Ω/m) and $q=IR^2$, equation (23) is worked out to be,

$$\lambda = 6.217 \frac{\ln 2}{\left(E_{60} - E_{30}\right)} \cdot \frac{0.04065}{4\pi} I^2 \tag{24}$$

where E_{60} and E_{30} are voltages to be measured. Because λ is not the target, the measured $I^2/\Delta E$ can be directly related to the gravimetric moisture content.

Specimens were aerated concretes with a bulk density of 500 kg/m^3 and the moisture content ranged from 0 to 150 kg/m^3 which corresponded to thermal conductivity of 0.1 to 0.4 W/mK. The supply current was determined to maximize the accuracy of voltage measure-ment at a given range of thermal conductivity. Results of the experiment is shown in Fig. 2.

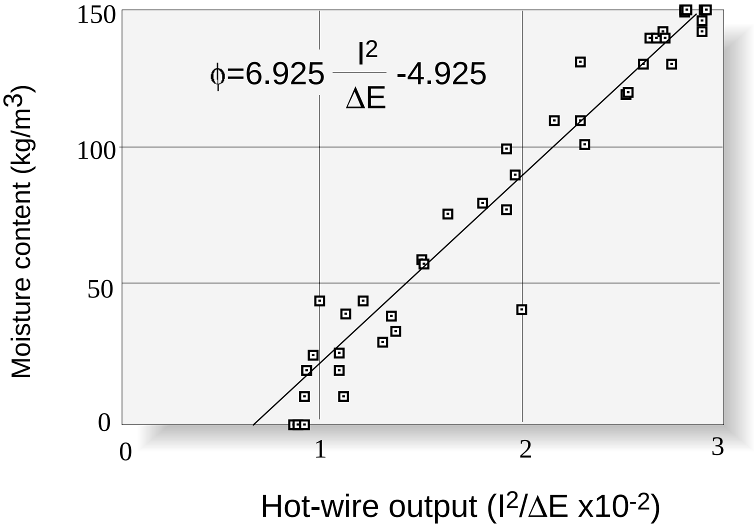

Fig. 2 An example of moisture content determination by the hot-wire method

3-3 Electric method

(1) Direct current resistance

A pair of electrodes embedded in a material, concrete for example, can be used to measure the direct current resistance between electrodes, which can be associated with the moisture content of concretes by way of the calibration curves. Electric resistance of the pure water, as well as the dry concretes, is quite high so that the major current carrier is ions dissolved in the pore water. Thus the direct current resistance measurement is subjected to inevitable influences of salts contained in concretes in addition to temperature and inhomogeneity of concretes. One degree of temperature results in the variation of resistance of 2 to 4 % and much larger at a high moisture region. However, the technique is very simple and suitable for the automatic and remote control. Timbers capable of having electrodes inserted from the surface are suited for this technique, which has been widely used in the timber drying industry. The resistance of wet timber varies over a range of 10^7 from the fiber saturation point to oven dry conditions and can be expressed experimentally in a linear relation,

$$\ln \rho = -K\varphi + c \tag{25}$$

where ρ is the resistivity and K and c are constants. This method has applied to concretes since the 1950s and is covering a practical range(29)(30).

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(29) Tabata, M., Koh, E. and Kamada, E., Measurement of moisture content by electric resistance method, Prep. Annual Meting AIJ (Tokai), 117-118, 1976 (in Japanese)

(2) Capacitance

Permittivity of water at a frequency of 1 GHz is 20 to 40 times larger than that of dry building materials for a wide range of temperature, and the permittivity is proportional to moisture content. Normally, permittivity can be determined by measuring the capacitance and by the following formula.

$$C = \frac{\varepsilon\varepsilon_v A}{d} \tag{26}$$

where C is the capacitance (F), ε is the relative permittivity of the surrounding medium in which charges are placed (F/m), ε_v is the relative permittivity of vacuum (F/m), A is the area of the parallel plate and d is the distance between the plates. Then the permittivity of wet materials can be given by,

$$\varepsilon_m = \sum_i \varepsilon_i v_i \tag{27}$$

where ε_m is the permittivity of porous materials, ε_i is the permittivity of the i th mass and v_i is its volume fraction. Frequency range used for this method is the radio waves of 1kHz to 1GHz and the influences of dissolved ions can be reduced at higher frequencies. Influences of temperature is relatively small. In general, relationship between capacitance and permittivity is not proportional, so that the calibration curves must be prepared, in the same way as the direct current resistance method, prior to determine the moisture content. The obtained moisture content is a volume fraction of water thereby the bulk density of the specimen must be known to obtain the moisture content by weight.

This method has been widely used to determine moisture content in soil and timber and many commercial instruments with a variety of probes are available. For concrete(31), a method to determine the capacitance using two frequencies(32) and a ceramics sensor to be embedded in concrete has been developed(33).

(3) Various electromagnetic waves

When microwaves with a frequency range of 1GHz to 100GHz are emitted to wet materials, they are largely attenuated by water molecules, especially at the frequency of 30GHz that is the specific relaxation frequency of water molecule. A commercial instrument using microwave transmission is available for process moisture control.

Because the absorption of infrared by water molecule occurs at particular wavelengths,

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(30) Nakane, S. et. al., Measurement of moisture content in concrete structure, Cement and Concrete (Japan), No. 473, 8-14, 1986 (in Japanese)

(31) Berg, A., Niklasson, G. A., Brantervik, K., Hedberg, B. and Nilsson, L. O., Dielectric properties of cement mortar as a function of water content, J. Appl. Phys., 71(12), 5897-5903, 1992

(32) Hudec, P., MacInnis, C. and Moukwa, M., The capacitance method of measuring moisture ans salt content of concrete, Cem. Concr. Res., 16, pp.481-480, 1986

(33) Kasai, Y. et. al., Measurement of moisture content of concrete by embedded ceramic sensors, Proc. Annual Meeting of JCI, 13(1), 397-402, 1991

original beam is separated into two beams with different wavelength by the filter, and are emitted to specimens to determine moisture content near the surface. Many commercial instruments are also available for the process control. This method has too high sensitivity to be interfered by trace contaminants on the surface.

3-4 Ultrasonic method

Determination of dynamic E-modulus and Poisson's ratio by measuring the ultrasonic pulse velocity has been specified in ASTM and other standards and widely used. Measuring technique is very simple but the results are influenced by the surface conditions of specimens where sensors are placed in close contact. Application of ultrasonic method has been widely studied(34) but measurement of moisture content for concretes is very few(35).

(1) Principle of measurement

Ultrasonic pulse velocity is influenced by the amount of moisture in materials. The sound velocity can be expressed as follows,

$$c = \sqrt{\frac{E}{d}} \tag{28}$$

where c is the sound velocity in the material (m/s), E is the Young's modulus of elasticity (MPa) and d is the bulk density of the material (kg/m^3). Taking apparent bulk density is a function of moisture content, we have,

$$d = \phi_s d_s + \phi_w d_w \tag{29}$$

where ϕ_s is the volume fraction of solid part of the material, ϕ_w is the volume fraction of moisture, d_s is the true density of material (kg/m^3) and is the density of water (kg/m^3). However, according to Plona and Johnson(36), who developed a theory of elastic wave propagation in saturated porous media of Biot, the sound velocity may be corrected with a factor α, that can be determined according to the frequency of the ultrasound and viscosity of pore water.

$$c = \sqrt{\frac{E}{\phi_s d_s + \phi_w d_w (1 - \alpha^{-1})}} \tag{30}$$

(2) Application

Specimens were autoclaved aerated concretes with bulk density of 500 kg/m3 and dimensions of 40 x40x160 mm, which were sandwiched by an emitter and a receiver with a

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(34) http://www.ndt.net/library/applic/concrete.htm

(35) Okajima, T. and Ichinose, K., Effects of moisture content on the rlastic modulus of concretes, Prep. Annual Meeting of AIJ, Kyushu, 173-174, 1981 (in Japanese)

(36) Plona, T. J., Johnson, D. L., Acoustic properties of porous systems: I. Phenomenological description, Physics and Chemistry of Porous Media, AIP conf. Proc. NO107, 89-104, 1984

distance of 40 mm. With measured values of an ultrasonic pulse velocity and a moisture content, the α value was determined as -2.80 for the aerated concrete.

$$c = \sqrt{\frac{196}{50 + 0.136\varphi}} \tag{31}$$

where c is the ultrasonic pulse velocity in the wet aerated concrete (km/s) and φ is the moisture content (kg/m^3). The semi-empirical formula satisfactory fits the measured values as shown in Fig. 3.

The dependency of ultrasonic velocity on moisture content for woods and aerated concretes shows negative correlation and the velocity decreases with the increase in moisture content. This means that the pore water doesn't contribute to the wave propagation but even damp it depending on ultrasonic frequency used and viscouisity of pore water(37). For mortar specimens, ultrasonic velocity increases with the increase in moisture content.

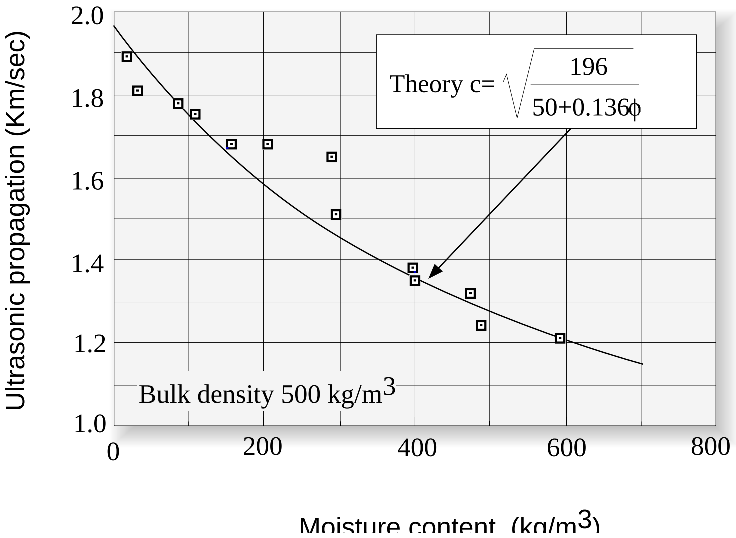

Fig. 3 An example of moisture content determination by the ultrasonic method

4 Equiriblium moisture content

Determination of equiriblium moistue content curves, the reationship between relative humidity and amount of adsorbed water, comprises two major techniques of relative humidity generation and weighing. When specimens are in vacuum, weighing can be made with micobalance(38)(39), quartz spring(40)(41) and berilium-copper cantilever(42)(43). Alternative methods without weighing uses volumetric loss of adsobete or micro-constant flow valve in the specimen

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(37) Sobue, N., Simulation study on stress wave velocity in wood above fiber saturaion point, J. Timber Society of Japan, 39(3), 271-276, 1993

(38) Willems, H. H., Poulis, J. A., Massen, C. H., Microgravimetric Measurements of Water Vapour Sorption on Hydrated Cement Pastes, Thermochimica Acta, 103 (1)137-145, 1986

(39) Fujimoto, S. and Inoue, H., Water vaapor adsorption on vicol glass, Journal of Chemical Engineering (Japan), 11(1), 41-47, 1985 (in Japanese)

(40) Matsumoto, M. and Matsushita, Y., Sorption-desorption behavior of aerated concrete in the hygroscopic range I - Verification of analysis based on the local equiriblium and linearmodel, Tans. AIJ, No. 302, 37-45, 1981 (in Japanese)

(41) Minahata, M. and Toyoda. Y., Measurement of equiriblium moisture content of building materials, Prep. Annual Meeting of AIJ, (Design and Planning), 1039-1040, 1986 (in Japanese)

(42) Sakota, A. et. al., Application of microcomuter to testing apparatus - Determinatin of sorption equiriblium andsorptionrate, Kagaku-Souchi, 24, 31-36, 1982

(43) Schuch, M. J. and Udell, K. S., A Study of the Thermodynamics of Evaporation and Condensation in a Porous System, Am. Soc. Mech. Eng. Heat Transfer Div., 46, 159-165, 1985

chamber of known volume. Relative humidity generation methods comprise saturated salt solution method as described in JIS Z 8806, temperature / pressure change method and flow division method. For smaller specimens, volumetric method that controls vapor pressures under the vacuum specimen chamber of knwon vokume has been used in the chemical engineerig(44)(45).

4-1 Relative pressure generation

(1) Saturated salt solutions

Relative humidites can be generated by the saturated salt solutions method at accuracy of 1% RH with special attentions to the temperature control and stirring in the chamber(46). In the tentative recommendation of measuring hygroscopic properties of building materials specified in JIS, one may sellect five saturated salt solutions out of seven and weigh specimens by a balance setled outside of the specimen chamber under atmospheric pressure and temperature of 20 ± 0.5 °C. Ohmi and Suzuki(47) measured woods and water absorbing polymers using entirely different salt solutions. Specimens were set in weighing bottles with cocks opened in decicators and weighed with the cocks shut. Both of the above methods may have problems with humidity disturbance at weighing. Decicators may be exposed to indoor environment in a short moment which cannot be recovered instantly resulting in a longer duration to equiriblium. Matsumoto and Matsushita(48) executed weighing in completely sealed specimen chamber using quartz springs, but the duration to equiriblium for a specimen took 40 days. Haggymassy(49) put specimens in weighing bottles and then in decicators under low pressure, where vapor diffusivity was increased associated with the increase in mean free path of water vapor in the decicator. This may contribute to both shortening of test duration and preventing carbonation for cementitous materials.

With all efforts of accurate temperature control, stirring and weighing in bottles, major drawack of this method is the limitation of available hummidity levels.

(2) Changing temperature or pressure

Commercial insturments based on the two-temperature method cannot be used for the determination of equiriblium moistue content because the lower limit of available relative humidity is as high as 30 % at a temperature of 20 °C. Availability of a saturator capable of generating saturated air at a temperature as low as 4 °C is unkown and no example of

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(44) Naono, H. et.al., Evaluation of particle surfaces and pore structure, Surface (Japan), 29(5), 364-375, 1991 (in Japanese)

(45) Miura, K. and Tanioka, M., An improved measurement of the water-vapor adsorption devised as one of the mutiple systm of indirect measurement, Applied Physics (Japan), 46(6), 589-596, 1977 (inJapanese)

(46) Kitano, H., Takahashi, T. and Inamatsu, T., A method to realize the humidity fixed points by saturated salt solutions, Bulletin of the Measurement and Control Socirty, 23(12), 1246-1253, 1987

(47) Ohmi, M. and Suzuki, M., Water vapor adsorption of woods and water absorbing polymers, Bulletin of Tokyo Agricultural University, No.22. 17-23, 1985

(48) Matsumoto, M. and Matsushita, Y., Sorption-desorption behavior of aerated concrete in the hygroscopic range I - Verification of analysis based on the local equiriblium and linearmodel, Tans. AIJ, No. 302, 37-45, 1981 (in Japanese)

(49) Haggymassy, Jr., J., Pore Structure Analysis by Water Vapor Adsorption, Department of Chemistry, Clarkson College of Technology, 1970

measurement was found. Ahlgren(50) built an apparatus based on the two-pressure method and determined a variety of isotherms for concretes, aeraated concretes, mortars, stones, bricks and various types of woods at seven points of relative humidities from 20 to 98 %.

(3) Flow division

Flow division method can generate a wide range of relative humidity rapidly, and continuous weighing from the outside of the specimen chamber can even be possible without affecting the chamber because the out flow of controlled air can be supplied continuousely giving stirring effect to the chamber.

Takahashi and co-workers(51) discussed the useage and precision of the flow-division humidity generator and concluded that the precision of relative humidity can be determined by the initial precison and degradation in time of the mass flow controller and overall precision was estimated to be ±1 to 2 % RH.

Fisher(52) pointed out the possibility of a generator with precision as low as 0.02% and resolution of 1 % by means of critical venturi nozzles of different fixed flow rates which subjected to flow addition by tree-way solenoid valves. In the flow division generator, the primary indoor air may be compressed by a compressor, dried by a molecular scieve dryer and supplied to flow controller as a dry air. Someshwar and Wilkinson(53) used nitrogen gas to simplify the aparatus. Tada(54) improved a commercial flow division generator to be controlled automatically by a microcomputer. A fully automatic sorption-desorption experiment was made for aerated concrete specimens.

The apparatus built in Bristol University(55) generates relative humidities by mixing dry and wet air. Two humidity sensors are needed to control fans and a damper that determine the mixing ratio and to confirm the humidity in the specimen chamber. Unlike the flow division method, the generated humidity must be confirmed by the humidity sensor thereby the precison entirely depends on that of the humidity sensor, and by its nature, change of large relative humidity difference in a short moment is impossible but it is suited for large specimens because it can work iwth a large volume of air.

(4) Changing vapor pressure in vacuum

Among many variations of this method, the volumetric method has been widely used and a variety of commercial instruments are available. In this method, the adsorbate (water)

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(50) Ahlgren, L.,Fuktfixering i Poroesa Byggnadsmaterial., Report 36, Division of Building Technology, The Lund Institute of Technology, 1972

(51) Takahashi, T., Inamatsu, T., and Kitano, H., Construction of a humidity ,generator by divided flow method, Bulletin of the Measurement and Control Socirty, 24(6), 557-562, 1988

(52) Fisher, R.S., An Accurate Flow-Division Humidity Generator, Proc. Int. Symp. Moisture and Humidity, 247-249, 1985

(53) Someshwar, A. V., Wilkinson, B. W., Study of Electric Field-Induced Effects on Water Vapor Adsorption in Porous Adsorbents, Ind. Eng. Chem. Fundam, 24 (2), 215-220, 1985

(54) Tada, S., Pore structure and moisture characteristics of porous inorganic building materials, in Advance in Autoclaved Aerated Concrete, Balkema, Rotterdam, 53-63, 1992

(55) Saidani-Scott, H. and Day, B. F., Measurement of Moisture Migration in Building Materials: Part 1, Experimental apparatus and Procedure, Part 2, Mathematical Analysis and Results, Proc. Int. Workshop on Mass-Ennergy Transfer and Deterioration of Building Components - Models and Characterisation of Transfer Properties, Paris, 295-321, 1995

is introduced step by step to the specimen chamber under vacuum and the amount of adsorbed water can be determined by the loss of adosorbate, vapor pressure and dead volume. In some appratuses, amount of adsorbate can be directly mesured without care of the dead volume of the vacuum system(56)(57).

4-2 Transient method

(1) Principle of measurement

Assuming that the rate of adsorption is proportional to the difference in amount of adsorbate between m_e in equilibrium and m at present, the rate of adsorption can be expressed in a following differential equation

$$\frac{dm}{dt} = \varphi\left(m_e - m\right), \tag{31}$$

where φ is a constant. By integrating equation (10), we have Langmur's adsorption equation

$$m = m_e(1 - e^{-\varphi t}), \tag{32}$$

which assumes an adsorption on a smooth free surface. The applicability of this equation to porous materials, whose rate-determining process may be diffusion, is therefore limited. The physical meaning of φ is a sum of sorption and desorption coefficients and it contains affinity information between adsorbed molecules and solid surfaces.

Watanabe and Shiligersky(58) proposed a method that can determine the equilibrium moisture content at an early stage by measuring the adsorption rate followed by a non-linear curve fitting that can determine $\mathrm{m_e}$ and φ at the same time. Taking into account of the hysteresis effect, different equilibrium moisture contents of m_{ea} and m_{ed}, for adsorption and desorption process respectively, under the same relative humidity were introduced as shown in Fig.4. With a known initial moisture content m_s on desorption, we have two rate equations describing the sorption and desorption processes

$$m = m_{\mathrm{ea}}(1 - e^{-\varphi t}), \quad m = m_s + m_{ed}(1 - e^{-\lambda t}). \tag{33}$$

If the necessary relative humidities for which respective equilibrium moisture contents should be known are 10, 20, 30 ...%, standard-dry specimens of the corresponding number must be prepared and subjected to a humidity change, for example, from 0 to 10% to estimate

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(56) Willems, H. H., Poulis, J. A., Massen, C. H., Microgravimetric Measurements of Water Vapour Sorption on Hydrated Cement Pastes, Thermochimica Acta, 103, (1)137-145, 1986

(57) Fujimoto, S. and Inoue, H., Water vaapor adsorption on vicol glass, Journal of Chemical Engineering (Japan), 11(1), 41-47, 1985 (in Japanese)

(58) Watanabe, K., Ashie, Y. and Shiligersky, I., Towards Paractical Simulation of Hygrothermal Behavior for Building Components, Part 3 Transient Mathod for Quick Measurement of Sorption Isotherm,Prep. Annual Meeting of Japan Air-conditioning and Sanitary Society, 29-32（Hiroshima）1995

an equilibrium moisture content of m_{ea}-10. The next specimen should be subjected to a humidity change from 0 to 20% to have an equilibrium moisture content of m_{ea}-20 and so forth.

(2) Application

The specimens were aerated concrete cut out from the bulk body. Relations between equilibrium moisture contents estimated from each experiment and respective relative humidities are also shown in Fig.5. All measurement took three days.

The results of the rapid measurement show good agreement with those measured by the conventional method. Because the principle of rapid method assumes a Langmur-type adsorption, it can be applicable to smooth surfaces, molecular sieves and highly porous materials whereas a modification of the equations may be necessary when this method is applied to dense porous materials.

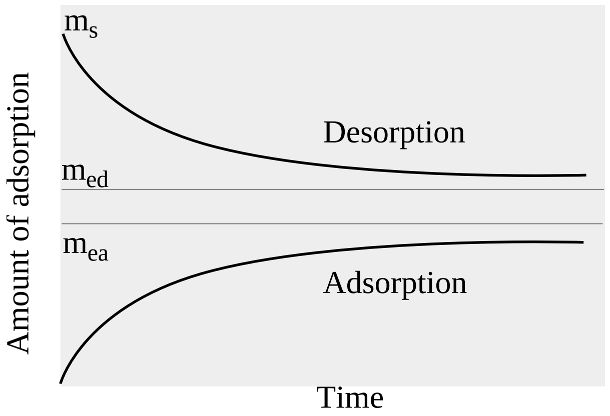

Fig. 4 Sorption-desorption equiriblium values

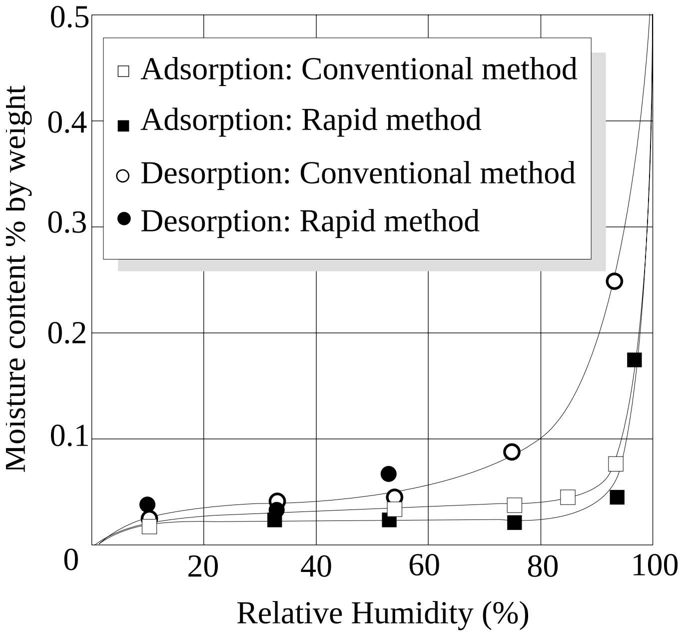

Fig. 5 Results of rapid sorption isotherm measurement

5. Moisture characteristics

Sorption isotherms, an apparent relation between relative humidity and equiriblium moisture contents of materials, give the relation between moisture contents of the material and chemical potentials of water at hygroscopic ranges. The relation at a high moisture content region is called the water retension curve that has been determined by the pressure plate method or pressure membrane method. The moisture characteristic curve is a combination of thses two moisture content ranges giving a relation between chemical potentials of water with respect to the free bulk water and moisture contents, and has been widely used in various application fields including soil science, plant physiology, food science and building science.

Penner(59) introduced the suction concept developed in soil science for the first time to the building science and showed measuring methods and water retension curves for spruce,

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(59) Penner, E, Suction and its use as a measure of moisture content and potentials in porous building materials, in Waxler, A. (editor) Humidity and Moisture, Vol. 4, Reinhold publ., 1965

whereas Sereda and Hatcheon(60) presented a result for autoclaved aerated concrete. Bomberg(61) widly applied knowledge of soil scinece to building materials and water retension curves, the capillary pressure-moisture content relation, of autoclaved aerated concretes, bricks and soft fiber boards were presented. The relationships between free energy of pore water and moisture contents of plastics foams were widely studied by Marechal(62), and of cellular concretes by Tada and Nakano(63).

5-1 Pressure plate method

When a wet material is subjected to a high, positive air pressure that is equal to a negative capillary pressure, water held in pores with a diameter larger than the Kelvin diameter corresponding to the capillary pressure will be released and driven by the gravity. The relationship between capillary pressure and moisture content, the water retension curve, can be determined by the relation of the air pressure and the amout of water that leaves the specimen. The pressure can be given by the Young-laplace equation,

$$P = -\frac{2\phi}{r}\cos\theta \tag{34}$$

where P is the air pressure (capillary pressure), r is the Kelvin radius, θ is the contact angle between solid and liquid and ϕ is the interfacial free energy of the liquid-gas interface.

Difficulties of the pressure plate method lie in introducing the exact amount of the released water to the outside of the system for gravimetric measurement. The pressure plate apparatus used in the Fraunhofer Institute of Building Physics has a rubber sheet underneath the porous plate to collect the released water(64). At a low pressure operation below atmospheric pressure, the released water can be directly driven downward by the suction. A review of the suction apparatus was given by Fagerlund(65). These methods are often called the dynamic water-expulsion method(66) and used for pore sturucture analysis(67). To automate the complicated measuring procedure, computer-controlled apparatuses were proposed(68)(69).

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(60) Sereda, P. J., Hatcheon, N. B., Moisture equilibrium and migration in building materials, ASTM Special Tech. Publ., 385, 1965

(61) Bomberg, M., Moisture flow through porous building materials, Lund Institute of Technology, Report 52, 1974

(62) Marechal, J-C., Propriete mehaniques et thermiques des mateialux isolants, Annales de l'institut techniques du baiment et des travaux publics, 301, 22-42, 1973

(63) Tada, S., Nakano, S., Microstructural Approach to Properties of Moist Cellular Concrete, Autoclaved Aerated Concrete -Moisture and Properties, ed. F. H. Wittmann, Elsevier, 71-88, 1983

(64) Kissel, K. and Krus, M., Experimental Determination of Building Materials Properties for Moisture Calculation, Proc. Int. Workshop on Mass-Ennergy Transfer and Deterioration of Building Components - Models and Characterisation of Transfer Properties, Paris, 322-342, 1995

(65) Fagerlund, G., Determination of Pore Size Distribution by Suction Porosimetry, Materials and Constructions,6(33) 191-201, 1973

(66) Gelinas, C. and Angers,R., Improvement of the Dynamic Water-Expulsion Method for Pore Size Distribution Measurement, Am. Ceram. Soc. Bull., 65(9)1297-1300, 1986

(67) Zager, L., Porengrosenverteilung nach dem Luft-Wasser-Verdrangungsverfahren. Auswertung der Messergebnisse mit Hilfe eines elektronischen Tischrechners, Ber. Dt. Keram. Ges., 55(1)13-17, 1978

(68) Shishido, I., Suzuki, M., A new measurement method of liquid transport porperties, Proc. Int. Symp. Drying, Vol.2, 764-768, 1984

5-2 Psychrometric method

Dew point measurement based on thermodynamical principle is suitable for determining the relative pressure ranging from 0.960 to 0.999. Thermocouple dew point psychrometer used for this measurement is an instrument prevailing in agricultural science(70). The measuring principle is as follows(71): the dew point drop ΔT is measured in such a way that one junction of a thermocouple in the probe is cooled down to the dew point temperature by Peltier effect, and the temperature difference with the other junction of the thermocouple is obtained by Seebeck effect.

For a mole of water vapor at a temperature T , dew point temperature Td and with high relative pressure P_s/P_s, both $\Delta P = P_s - P_s$ and $\Delta T = T - T$d are sufficiently small, then clausius-Clapeyron equation gives

$$\frac{\Delta P}{\Delta T} = \frac{\Delta H}{TV_g} = \frac{P_s \Delta H}{RT^2} \ , \qquad (35)$$

where V_g is the volume of water vapor which is larger enough than that of water, ΔH is the enthalpy change associated with the phase transition of water and the relation of ideal gas $P_s\, V_g = R\, T$ is used.

The thermoelectromotive force E of the thermocouple wired between the cooled junction and the normal junction with a coefficient ε can be written as

$$E = \varepsilon \Delta T = \varepsilon\left[RT^2/\Delta H\right]\left[\left(P_s - P\right)/P_s\right] = \varepsilon\left[RT^2/\Delta H\right]\left(1 - P/P_s\right) \ . \qquad (36)$$

Substituting P/P_s by $\exp(-\Delta\mu/RT)$ in eq.37 gives

$$\begin{aligned} E &= \varepsilon\left[RT^2/\Delta H\right]\left[1 - \exp\ (\Delta\mu/RT)\right] \\ &= \varepsilon\left[RT^2/\Delta H\right]\left[(\Delta\mu/RT) - (\Delta\mu/RT)^2/2!\right] \cong \varepsilon T \Delta\mu/\Delta H \end{aligned} \qquad (37)$$

If the vapor pressure does not vary, the enthalpy change ΔH associated with the phase transition of water does not depend on temperature and ΔT is small, chemical potential of water vapor, as well as that of water in materials, is thus approximately obtained from the dew point depression. The measurable range is -5 x 10^3 ~ -10^2 (J /Kg) depending upon both cooling capacity and accuracy in the measurement of microvoltage.

5-3 Tada method

Conventional methods are generally time-consuming and lack theoretical backbone when the data obtained by different methods are connected. This method extends water

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(69) Boels, D., van Gils, J. B. H. M., Veerman, G. J. and Wit, K. E., Theory and systems of automatic determination of soil moisture characteristics and unsaturated hydraulic conductivities, Soil Science, 126, 191-199, 1978

(70) Richards, L. A., A thermocouple psychrometer for measuring the relative vapor pressure of water in liquid or porous materials, in Wexler, A. ed., Humidity and Moisture, vol.4, Reinhold publ. Co. NY, 13-18, 1965

(71) Tada, S., Pore structure and moisture characteristics of porous inorganic building materials, France-Japan workshop on simultaneous heat and moisture transport, Tokyo, 19p, 1991

vapor adsorption over wide ranges that can be covered by mercury intrusion technique(72).

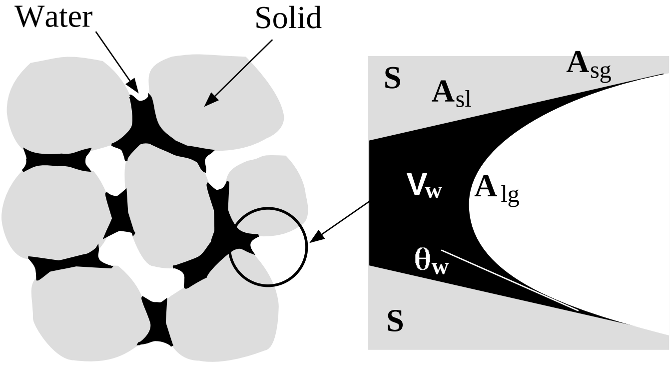

Fig. 6 A model of water vapor adsorption

(1) Water vapor adsorption

A general theory of gas adsorption without regard to particular pore geometry has been presented as the Modelless method by Brunauer and co-workers(73). However, a more general formulation with rigorous definition of thermodynamic system is necessary to represent pore structural profile in conjunction with the other method such as mercury injection porosimetry.

In the measurement of water vapor sorption isotherm, amount of adsorbed water is measured in accordance with changes in relative pressure P/Ps , i.e. the ratio of saturated vapor pressure Ps at the temperature with respect to the actual vapor pressure P.

We will consider a thermodynamic system composed only of moisture in a material (denoted as l and g for liquid and gas phase respectively) under normal atmospheric pressure as illustrated schematically in Fig. 6. Under constant absolute temperature T and total pressure of the system P, changes in interfacial Gibbs free energy of adsorbed water and solid *sl*, water vapor and solid *sg* and adsorbed water and water vapor *lg* will take place as moisture comes into the system associated with changes in relative pressure. The total differential of Gibbs free energy of the system is given by (74),

$$dG = - SdT + VdP + A_{sg} d\Phi_{sg} + A_{sl} d\Phi_{sl} + A_{lg} d\Phi_{lg} + \mu_w dn, \tag{38}$$

where *S* is entropy of the system, *V* is volume of the system, *A* is surface area of interface , Φ is interfacial tension and μ_w is chemical potential of water given by RTln(P/Ps) with respect to isothermal pure bulk water. R is the gas constant and n is the number of mole of water which approach the system. we have dn=dV/v with V for the volume of the newly adsorbed water and v for the specific volume of water.

When the system reach equilibrium condition (dG=0) isothermally (dT=0) under constant atmospheric pressure (dP=0), terms representing reversible work are only present in eq.39;

$$A_{sg} d\Phi_{sg} + A_{s\,l} d\Phi_{sl} + A_{lg} d\Phi_{lg} + RTln(P/P_s) \cdot dV/v = 0. \tag{39}$$

If we assume that Φ_{lg} can vary associated with adsorption while change in Φ_{sl} is negligible, $d\Phi_{sl}$ can be set as zero. Differentiating Young-Dupre equation $\Phi_{sg} = \Phi_{sl} + \Phi_{lg}$

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(72) Tada, S., Pore structure and moisture characteristics of porous inorganic building materials, in Advance in Autoclaved Aerated Concrete, Balkema, Rotterdam, 53-63, 1992

(73) Brunauer, S., Skalny, J., Odler, I., Complete Pore Structure Analysis, Proc. Int. Symp. Pore Struct. Prop. Mater., 6Vols, Academia, Prague, C3-C26, 1973

(74) Dufay, R., Prigogine, I., Bellemans, A., Everett, D. H., Surface Tension and Adsorption, Wiley, p.54, 1966

cosθw gives $d\Phi_{sg}= d\Phi_{lg}\cos\theta_w$, where qw is contact angle between adsorbed water and solid. Then eq.39 can be written as

$$(A_{sg}\cos\theta_w+A_{lg})d\Phi_{lg} + RT\ln(P/P_s) \cdot dV/v = 0 . \qquad (40)$$

Substituting $A_{sg}\cos\theta_w+A_{lg}$ by **A**, **A** represents interfacial area which undergoes actual change associated with the progress of adsorption and condensation of adsorbate. Integration of eq.41with initial condition of V=0 and $\Phi_{lg}=0$ at the start of adsorption, and $\Phi_{lg}=\Phi_w$ at $V=V_w$, gives a generalized Kelvin equation,

$$\frac{RT\ln(p/p_s)}{v} = -\frac{\Phi_w}{R_H} \qquad (41)$$

where Φ_w is surface tension of water and RH is hydraulic radius defined as V_w /**A**; volume of adsorbed water divided by effective surface area.

In this derivation, any configuration or phase geometry between adsorbete and capillary condensate is not assumed. At the initial stage of adsorption below monolayer, it is proper for Φ_{lg} to be zero. When progress of adsorption extends over the hindered adsorbed region where free adsorption of water molecule is difficult and over the capillary condensation region, A_{sg} becomes zero and dA_{lg} is negative, and subsequently, A_{lg} will approach the apparent surface area of the specimen. The area **A** $(=A_{sg}\cos\theta_w+A_{lg})$ has a finite value though it is negligibly small compared to the specific surface area inside of the specimen, and RH will not become infinite when P/Ps approaches to 1.

(2) Mercury injection

Derivation of a generalized equation for mercury injection techniques, as Kiselev equation for gas adsorption quated by Brunauer, has been made by Rootare and Prenzlow(75). Because the aim of the equation was to calculate specific surface area, generalized formulation for mercury injection techniques without any pore geometry could not be derived.

We will consider a thermodynamic system composed only of mercury inside and outside (superscript i and o) of a specimen as illustrated schematically in Fig.7.

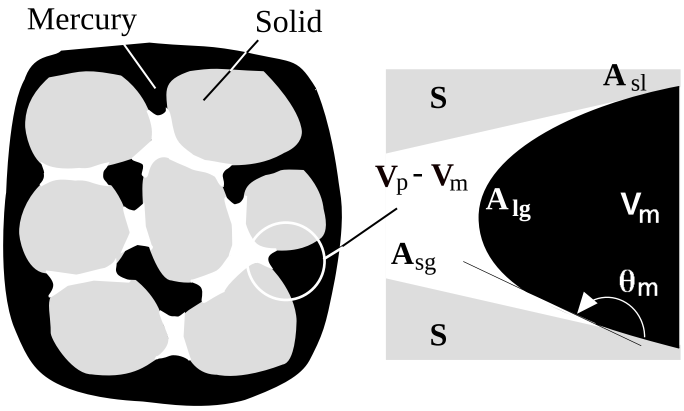

Fig. 7 A model of mercury injection

In the procedure of mercury injection to specimen, intruded volume of mercury dV can be measured with respect to the pressure P, by which area work between mercury and specimen (solid phase denoted as *s*) will be done. The total differential of Helmholz free

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(75) Rootare, H. M., Prenzlow, C. F., Surface Area from Mercury Prosimeter Measurements, J. Phys. Chem., vol. 71, pp.2733-2736, , 1967

energy of the system is given by (76),

$$dF = -SdT - P^o dV^o - P\,dV - P_g dV_g + \Phi_{lg} dA_{lg} + \Phi_{sg} dA_{sg} + \Phi_{sl} dA_{sl} + \mu dn. \qquad (42)$$

With an assumption of constant volume of mercury in liquid phase $dV_{il}+dV_{ol}=0$ can be given. Since the pore volume and the internal surface area of the specimen are constant, $dV_{ig}+dV_{il}=0$ and $dA_{s\,g} + dA_{s\,l} = 0$ can be held respectively.

With contact angle between mercury and the solid surface θ_m , Young-Dupre equation gives $\Phi_{sg}-\Phi_{sl}=\Phi_{lg}\cos\theta_m$. Since no mass comes into the system, dn is equal to zero and when the system approaches isothermally (dT=0) to an equilibrium condition (dΦ=0), we have

$$(P^o - P + P_g)\, dV_l + (dA_{lg} + dA_{sg}\cos\theta_m)\Phi_{lg} = 0, \qquad (43)$$

where we can set $P_{ol}=P_{il}=P_{ig}=P$ and $dV_{il}=dV$, and A_{lg} can vary from a constant value "a", which is nearly equal to an apparent surface area of the specimen, to A_{lg} associated with change in V from 0 to V_m . Integration of eq.43 with these initial condition gives

$$PV_m = -\Phi_{lg}(A_{lg} + A_{sg}\cos\theta_m) + a\,, \qquad (44)$$

where a is negligibly small. Substituting $R_H = V_m / A'$ with $A' = A_{lg} + A_{sg}\cos\theta_m$ in eq.44, we have

$$P = -\Phi_m / R_H\,, \qquad (45)$$

where Φ_m is interfacial tension between mercury and vapor of mercury.

Above formulation is generalized Rootare and Prenzlow equation and can be a modelless theory of mercury porosimetry.

During the water vapor adsorption, eq.41 is valid and RH and Vm can be obtained by measurements of relative humidity and weight of specimen. Naturally, the finer the pore is,the sooner it is filled with adsorbed water. During the mercury injection, on the other hand, eq.46 is held and amount of mercury injected up to the pressure P can be measured, when the coarser the pore is the sooner it is filled with mercury. To combine these two techniques for the wide range pore-size analysis, we assume relationships between V_w and V_m, θ_w and θ_m at any R_H as follows;

$$V_w + V_m = V_p\,, \quad \theta_w + \theta_m = \pi, \qquad (46)$$

where V_p is the total porosity of the specimen which can be easily known by vacuum saturation method.

The left side term in eq.41 is negative disjoining pressure which is denoted as Π, and at the same R_H , the hydrostatic pressure of mercury P in eq.45 can be translated to the disjoining pressure of adsorbed water as follows,

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(76) Tada, S., Tanaka, M., Matsunaga, Y., Measurement of Pore Structure of Aerated Concrete, Proc. Beijing Int. Symp. Cem. Concr., vol.3, , 384-393, 1985

$$\Pi = P \cdot \Phi_w / \Phi_m \quad . \tag{47}$$

The amount of adsorbate corresponding to V_m at the disjoining pressure Π can be calculated from V_p -V_m . Consequently, the wide range water vapor sorption isotherm can be obtained, and hence the chemical potential of water at a given moisture content is derived.

6 Water vapor diffusivity

6-1 Cup method

The cup method has been widely used as a standard method specified in many coutries such as ASTM in USA(77). An water vapor absorbing material is enclosed in the cup, with 60 mm Φ in diameter and 15 mm in depth as specified in JIS. Water vapor flows throuth the specimen changing the total weight and its steady state increase or decrease gives a water vapor diffusivity. Considerable time may be taken for hygroscopic and thick specimens, like many building materials, to reach the steady state.

Major error factors are a bypass flow at the perimeter of a thick specimen where one dimensional flow is nomore assured, and the reproducibility of the surface vapor conductance for which a correction method has been proposed(78). Examples of measurement of water vapor diffuivity with the cup method for cementitous materials are vary few(79).

6-2 Two -box method

Two different water vapor absorbing materials, creating a vapor pressure difference, are put into two boxes in contact with each other with a specimen between them. Continuous measurement of the change in weight of the water vapor absorbing materials may confirm the steady state condition when the vapor diffusivity ican be calculated. The principle of this method is the same as the cup method but specimens with larger dimensions can be measured and hence the one dimensionality of vapor flow is improved. Circulation can be applied within the box to minimize the error due to surface vapor conductance. A fatal drawback is a lack of standard in the construction of apparatus, which are different laboratory to laboratory resulting in a disagreement of their test results. Ohsawa(80) compared a variety of two box apparatus in detail.

6-3 Sorptivity method

(1) Principle of measurement

The mass balance equation (12) can be simplified when the liquid flux is negligible and the vapor diffusivity $D_{\theta V}$ is not widely dependent on moisture content. In isothermal conditions, we have a following equation (48), which has a solution for a semi-infinite medium with a plane, continuous source c_i kg/m^3 applied to the boundary of the medium x=o, t>0 at an initial condition of c_o throughout x>o, t=0

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(77) Joy, F. A. and Wilson, A. G., Standardization of the dish nethod for measuring water vapor transmission, Int. Symp. Humidity and Moisture, Washington DC. (4), 259-270, 1963

(78) Andersson, A-C., Verification of calculation methods for moisture transport in porous building materials, Document , Swedish Council for Building Research, D6:1985, 223P

(79) Kari, B., Perrin, B. and Foures, J. C., Perméabilité a la Vapeur d'eau de Materiaux de Construction: Calcul Numerique, Materials and Constructions, 24, 227-233, 1991

(80) Ohsawa, T., Water vapor transfer measurement method for building materials, 6th Workshop of heat subcommittee in building environmant committee in AIJ, 39-46, 1976 (in Japanese)

$$\frac{\partial \theta}{\partial t} = D_{\theta V} \frac{\partial^2 \theta}{\partial x^2}. \tag{48}$$

The total amount of moisture W in kg/m^2 that has left the medium at time t (s) can be expressed as

$$W = 2(c_i - c_0)\left(\frac{\overline{D}_{\theta V} t}{\pi}\right)^{\frac{1}{2}}, \tag{49}$$

where c_i is a moisture content corresponding to a relative humidity subjected to change as a test condition and c_o is a moisture content corresponding to a relative humidity of the initial state of the medium. $\overline{D}_{\theta V}$ is a mean vapor diffusivity at moisture content between c_i and c_o.

From eq. (49), the vapor conductivity $\overline{D_V}$ at this moisture content rage works out to be

$$\overline{D_V} = \frac{\pi}{4(c_i - c_0)^2 p_{VS}} \left(\frac{\partial \theta}{\partial h}\right)\left(\frac{W}{\sqrt{t}}\right)^2. \tag{50}$$

Experimental procedure is, at first, to change the relative humidity around the medium instantly and to keep it to be in constant, then the change of mass of the medium should be plotted against square root of time to have the gradient. The $\partial\theta/\partial h$ should be measured separately as a gradient of the sorption isotherm.

This measurement principle comprises some important assumptions. First, the surface moisture transfer resistance is neglected. Next, the medium is not actually semi- infinite. Finally, the dependency of the vapor conductivity on moisture content is very small. Nakao and Ooshima (81) estimated the possible error and showed necessary test conditions to put the error within a permissible range.

(2) Application

Measuring apparatus comprises a flow-division relative humidity generator, an electronic balance and a notebook computer. The electronic balance should have a maximum weighing capacity of 260 g, a resolution of 1 mg and a RS-232C out-put. Changes of mass of a specimen according to the change of the ambient relative humidity are measured by the electronic balance and

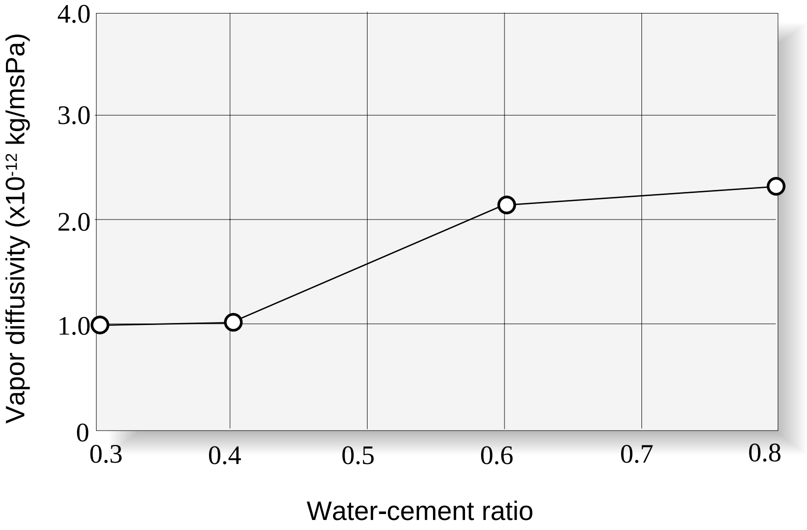

Fig. 8 Water vapor diffusivity of concrete

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(81) Nakao, M. and Ohshima, K. 1982: Dynamic method for measuring moisture properties of building materials, Research Paper of AIJ, No. 315, 76-82 (in Japanese)

send in every 60 seconds to the computer.

The specimens were concretess with water cement ratio (W/C) of 0.3, 0.4, 06 and 0.8. The temperature of the specimen chamber was 293 K throughout the experiment. After setting a specimen equilibrated under a relative humidity of 60%, the relative humidity in the chamber was changed to 90% and kept in constant.

The change of mass was measured in every 60 seconds, divided by the area of the open surfaces and plotted against square root of time. The results show similar tendency with those measured with the cup method for cement mortars having an equal range of water cement ratio and relative humidity as shown in Fig. 8(82).

7 Water conductivity

A term of water conductivity has been often used in the building science instead of unsaturated hydraulic conductivity used in the soil science. Recent theory and measuring thechniques of water conductivity were dealt with by Jentz(83).

7-1 Moisture profile methods

If the liquid flux and moisture content distribution in the specimen are obtained at the same time, the water conductivity $D_{\theta L}$ can be calculated from the flux equation

$$\mathbf{J}_L = -D_{\theta L}\nabla\theta . \tag{51}$$

Two methods for measuring the liquid flux have been reported.

Kooi(84) and Matsumoto(85) applied horizontal water input to a cylinder specimen to minimize the gravity effect, and the flux was determined from a moving menisci in a measuring pipet connected to a water tank. When the inflow reached a steady-state conditions, specimen was cut into pieces and the moisture distribution was determined. Water water conductivity obtained with this method is in a narrow moisture content range and is limited only to an absorption process.

Jonell and co-workers (86) executed a vertical water uptake test for specimens and cut one of them into pieces consecutively at a specified period to determine moisture content distributions. The water fluxes were calculated from the overall mass increase and moisture contents of each cut pieces. This method, unnecessary to wait until a steady-state condition, is more rapid and can cover wider moisture range by taking a longer period for cutting a specimen. However, the specimen may be limited to easy-to-cut materials and the result may scatter because the results of different specimens are combined in a single curve.

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(82) Okawara, O., Kasai, Y., Matsui, I., Yuasa, N. and Tada, S., Quality of cover concretes - Hygroscopic properties, Proc. Annual Conference of College of Industrial Technology, Nihon University, 1997 (in Japanese)

(83) Janz, M., Methods of measuring the water diffusivity at high moisture levels, Thesis, Lund Institute of Technology, TVBM-3076, 1997
http://www.ldc.lu.se/lthbml/e-doc.htm

(84) Kooi, J. van der, Moisture transport in cellular concrete roofs, Proc. 2nd Int. Symp. Moisture Problems in Building, Rotterdam, 2.5.5, 1974

(85) Matsumoto, M., A Study on Simultaneous Heat and Moisture Transport and Moisture Accumulation in Building Walls, Thesis of Kyoto University, 1978 (in Japanese)

(86) Jonel, P., Karamustafaoglu, V., Tepfers, R., Determination of the coefficient of capillary flow for steam-cures lightweight concrete, Rilem Symp. Lightweight Concrete, Goteborg, 433-437, 1960

The second method, having a problem in accuracy, has an advantage of simplicity without a need of equipments, thereby the measuring principle is described in detail.

(1) Wetting process

Assume prism specimens with dimensions of 40 x 40 x 160, having notches for a quick cut, are conditioned under 20 °C and 98% of relative humidity for a week, and are put in a shallow water bath with an open end of a specimen in contact with water whereas the other side of the specimen are sealed. After 1, 2, 3, 4, 6, 8, 15 and 20 days of water uptake, each one specimen is taken, weighed and then cut into *n* pieces, and weighed again to determine each moisture content.

Let the mass of the *k*th piece is q_k, its standard dry mass is q_{kd}, and its volume is *v*, then the volumetric moisture content θ_k of the piece is (q_k, - q_{kd},)/*v*. With a cross section of the specimen *A* and the duration of water uptake for the specimen *Δt*, the liquid flux for the *k*th piece is $\sum_{i=k}^{n}\left(q_i - q_{di}\right)/A\Delta t$. The water conductivity $D_{\theta k}$ can be expressed as

$$D_{\theta k} = \frac{\sum_{i=k}^{n}\left(q_i - q_{di}\right)/A\Delta t}{\left(\frac{\theta_k - \theta_{k+1}}{\Delta x}\right)}. \tag{52}$$

(1) Drying process

Measurement of water conductivity in the drying process requires the same number of specimens. All specimens may be saturated with a tap water in the vacuum saturator, sealed all side except for one open end with aluminum foil and subjected to drying under a constant temperature and relative humidity. The subsequent processes are the same as the wetting test.

7-2 Bolzmann transformation method

This method applies Bolzmann transformation to the mass balance equation under isothermal conditions.

$$\nabla(D_\theta \nabla\theta) + \rho_L \frac{\partial\theta}{\partial t} = 0. \tag{53}$$

With an intial and a boundary condition of $\theta = \theta_0$, at x=0, and $\theta = \theta$ at any x at t=0, introducing Bolzmann parameter $\lambda = x/\sqrt{t}$ to equation (53) gives a following ordinary differential equation,

$$\frac{d}{d\lambda}\left(D_\theta \frac{d\theta}{d\lambda}\right) + \frac{1}{2}\lambda\frac{d\theta}{d\lambda} = 0 \tag{54}$$

that has a solution of $x(\theta,t) = \lambda(\theta)t^{1/2}$ type(87). By integrating theequation (54), D_θ is can be expressed(88) as,

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(87) Philip, J. R., Theory of Infiltration, Adv. Hydrosci., 5, 215-296, 1969

(88) Bruce, R. R. and Klute, A., The Measurement of Soil Moisture Diffusivity, Soil Sci. Soc. Am. Proc. 20, 458-462, 1956

$$D_\theta = -\frac{1}{2}\left(\frac{d\lambda}{d\theta}\right)\int_{\theta_0}^{\theta} \lambda d\theta. \tag{55}$$

By measuring distributions of moisture content at each time, relations betrween θ and λ can be obtained, and the D_θ can be determined by calculating $(d\lambda / d\theta)$ and the integral term. This method has a wide variety of applications, including error analysis(89), even regarded to construction materials.

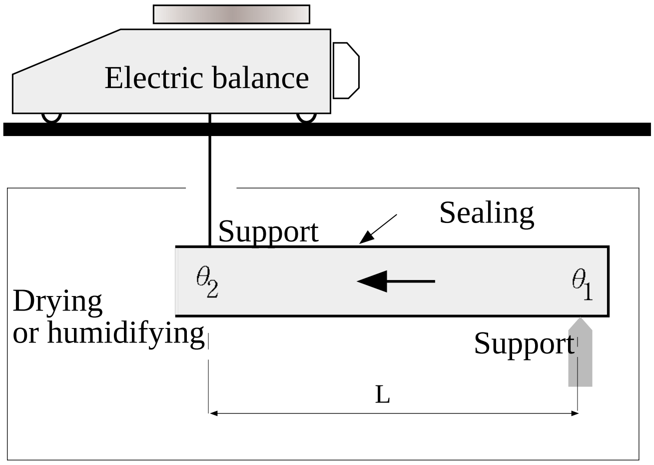

Fig. 9 Moment method

7-3 Moment method

Claesson and Gaffner(90) developed a method that can determine water conductivity without measuring moisture profiles nor water flux. A specimen of length L and cross section of A is conditioned to have a moisture content of θ_1 , and all sides of the slecimen may be sealed except for one side subjected to drying to have an equiriblium moisture content of θ_2. The specimen is supported in a manner as shown in Fig. 9, and the weight changes are measured continuouesely. After the steady state of water flow is established, relationship between the gradient of the change in weight *dm/dt* and the D_θ can be expressed as follows,

$$\frac{dm}{dt} = -\frac{A}{L}\int_{\theta_1}^{\theta_2} D_\theta(\theta) d\theta \cong -\frac{A}{L} D_\theta \Delta\theta, \tag{56}$$

where it is assumed that the difference between θ_1 and θ_2 is sufficiently small enough to take D_θ as constant. Then the D_θ is given by,

$$D_\theta = -\frac{L}{A(\theta_2 - \theta_1)} \cdot \frac{dm}{dt}. \tag{57}$$

Measurement of D_θ, at the average moisture content of θ_1 and θ_2 , has been applied to aerated concretes and bricks(91).

7-4 CSTB method

Specimens are placed between two container filled with polyethylene glycols solutions

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(89) Wang, B-X. and Fang, Z-H, Water Absorption and Measurement of the Mass Diffusivity in Porous Media, Int. J. Heat and Mass Transfer, 31 (2) 251-257, 1988

(90) Claesson, J. and Gaffner, D., Fukt i Porosa Byggnadsmaterial, Report 1977.1, Lund Institute of Technology, 1977

(91) Andersson, A-C., Verification of calculation methods for moisture transport in porous building materials, Document , Swedish Council for Building Research, D6:1985, 223P

of different concentrations by which a chemical potential gradient is created. Because the solutions are in contact with the specimen through a semi-permeable membrane, only water can migrate from the solution of lower concentration to the other of higher concentration, and the amount of water that moved can be determined by comparing the difference in water levels. Because the amount of each solutions are sufficiently large, change in concentratons due to the migration of water is negligible. Then the water flux can be expressed as,

$$\mathbf{J}_L = -D_\mu \frac{RTd\ln\left(c_1 / c_2\right)}{dx}, \qquad (58)$$

where D_μ is a water conductivity when the chemical potential gradient of water is used as a driving force, c is the molar concentration of the solution. This method has a couple of advantages. The chemical potential gradient can be applied directly by the difference in concentrations of polymer solutions so that no other driving forces, such as vapor pressure and gravity, can be mixed up. The water conductivity can be determined as a function of moisture content when combinations of each two concentrations, and respective equilibrium moisture contents, are appropriately chosen. The apparatus is very simple and requires no.special operation techniques(92).

8 Conclusions

To date, prediction of moisture properties from the microtructural data or from its theoretical model has not always resulted in success. Therefore, experimental studies may be indispensable at present. However, by taking accout of cross coupling with heat, electoricity and other masses, even hard-to-measure tranport coefficients may be determined theoretically, or the measurement itself may become much easier. This can be a study for the future.

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(92) Duforestel, T. and Miquel, A., Advanced Hygrometric Measurements, Proc. Int. Workshop on Mass-Ennergy Transfer and Deterioration of Building Components - Models and Characterisation of Transfer Properties, Paris, 365-385, 1995