

A Dynamic Method Determining Equilibrium Moisture Content of Porous Materials

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Abstract

Equilibrium moisture content is an important moisture characteristics of porous materials, but its determination has required considerable time and care and the judgement of equilibrium may eventually be arbitrary. Dynamic method that can predict the equilibrium moisture content by curve-fitting to sorption kinetics experiments was proposed in the absence of accuracy consideration. We have examined the kinetic equations and measurement conditions of the dynamic method, which was applied to hardened cement pastes and aerated concrete. Results showed good agreement with those measured by the conventional saturated salt solution method and volumetric method.

1. Introduction

Relationship between the concentration of a mass in a porous material isothermally in equilibrium with that in the environment is called sorption isotherm. When the mass is water, the relation between atmospheric relative humidity and equilibrium moisture content of materials is the water vapor sorption isotherm, which is an indispensable material property when studying moisture behavior of porous hydrophilic materials such as cement-based materials. Especially in moisture transport analysis, moisture capacity that can convert the chemical potential gradient or relative humidity gradient into moisture content gradient, can be obtained from the water vapor sorption isotherm. As the name implies, it takes so long time to obtain "equilibrium" values that difficulties of changes in material properties may arise.

For simplicity, the scope of this study was limited to the isothermal water transport and to the hygroscopic moisture content range. Specimens comprised hardened cement pastes, HCP, having different water-cement ratios, mortars and an aerated concrete, AAC. Stepwise changes in relative humidity were applied to the specimens and the adsorption rates were recorded continuously. The adsorption rate at a stepwise change in relative humidity was fitted to an analytical solution of the diffusion equation at the boundary condition resulting in the rapid estimation of an equilibrium moisture content at the relative humidity.

2. Principle of measuring method

2.1 Conventional methods

A correct equilibrium moisture content can be obtained when a relative humidity is accurately generated and the adsorbed mass is continuously weighed. Standard methods of relative humidity generation include the saturated salt solution method, flow-division method that mixes dry and saturated air and the method altering temperature or pressure or both. The volumetric method that isothermally changes the vapor pressure in a vacuum system has been widely used in the chemical engineering laboratory.

The saturated salt solution method can produce a relative humidity with a precision of 1 percent when the container of the salt solution is stirred and the temperature is controlled carefully [1].

Haggymassy [2] combined weighing bottle with saturated salt solutions under vacuum and determined isotherms of hardened cement pastes. The mean free path of water vapor decreases under vacuum leading to an increase in its diffusivity in air. This reduces the time to reach an equilibrium and is effective in preventing carbonation of cement based specimens. Yuasa and co-workers [3] ground specimens into powder and introduced stirring mechanism in a saturated salt solution container. With all these means, the saturated salt solution method has an disadvantage of generating limited number of relative humidities. This method, as well as the volumetric method, is a standard with its simplicity, and is placed as the reference method of this study.

The flow-division method can generate a wide range of relative humidities. Because the conditioned air flows continuously, the specimen chamber can be stirred and need not be a closed space making it easy to monitor the specimen weight, for instance by an electronic balance from outside of the system. Takahashi and co-workers studied measuring conditions and precision of the flow-division humidity generator [4]. It was shown that the overall precision is dominated by that of the mass flow controllers and their change in performance with time, and that the precision falls in a range of 1 to 2 percent when employing the approximate formula specified in JIS Z 8806.

In this study, a commercial flow-division humidity generator was calibrated by a dew hygrometer to have a flow-ratio table specific to the generator enabling of running at a precision more than plus or minus 1 percent, and the computer controlled electric balance was used for a fully automated measuring system. Thus the apparatus can maintain a precise humidity for a long time and, during the long period of adsorption rate monitoring, one may obtain a moisture content as close as possible to the equilibrium moisture content. Results in a practically permissible duration, however, may only be obtained on the basis of a completely new prediction model.

2.2 Principle of the dynamic method

In the equation of continuity of water in porous media, water diffusivity D_θ is normally a function of the moisture content θ . In this experiment, the equation is taken as linear because an adsorption experiment will be executed under a constant relative humidity. For a sphere with a radius r , the water balance equation may be given by

$$\frac{\partial \theta}{\partial t} = D_{\theta} \left(\frac{\partial^2 \theta}{\partial r^2} + \frac{2}{r} \frac{\partial \theta}{\partial r} \right) \quad (1)$$

which can be converted to the one dimensional linear equation by substituting θ with u/r . The initial and the boundary conditions are that the surface moisture content of a sphere with a radius R , or relative humidity in equilibrium with the moisture content, is always constant and that the initial moisture content of the sphere in the beginning of adsorption is zero,

$$\begin{aligned} u=0, \quad r=0, \quad t>0 \\ u=R\theta_0, \quad r=R, \quad t>0 \\ u=0, \quad 0<r<R, \quad t=0. \end{aligned} \quad (2)$$

With variables separation method, the following formula is obtained [5],

$$m(t) = m_e \left[1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 kt) \right] \quad (3)$$

where $m(t)$ is the total mass passed from the surface of a sphere in a finite time, m_e is the total mass

passed after the infinitely long time and k is $D_0\pi^2/R^2$.

These initial and boundary conditions can be attained by providing the following experimental conditions: the specimen is kept under a 0 percent relative humidity for a sufficiently long time, and then the specimen is introduced in the specimen chamber of the humidity generator where a specified relative humidity is continuously supplied. In the equation (3), a $n=5$ polynomial may be a good approximation at an early stage of adsorption while $n=1$ may be a good approximation at all the stage, including the latter stage, of adsorption. Thus executing the adsorption experiment of a spherical specimen and determine a , b and c in the following equation by non-linear curve fitting at a sufficiently high correlation coefficient, it is possible to predict the equilibrium moisture content θ_e by dividing a with the standard dry mass.

$$m(t) = a[1 - b \exp(-ct)] \quad (n=1) \quad (4a)$$

$$m(t) = a \begin{bmatrix} 1 - b \exp(-ct) - 0.25b \exp(-4ct) \\ -0.1b \exp(-9ct) - 0.0625b \exp(-16ct) \\ -0.04b \exp(-25ct) \end{bmatrix} \quad (n=5) \quad (4b)$$

The equilibrium moisture content differs depending on adsorption or desorption while only adsorption process was considered in this study.

The reason why the equilibrium moisture content appears in the rate equation can be explained as follows. The specimen is kept under constant zero relative humidity for a sufficiently long time resulting in having an uniformly zero moisture content. When the ambient relative humidity changes into a constant value h and is maintained, a thin layer with a moisture content in equilibrium with the relative humidity h may appear immediately. The total amount of moisture entering in the specimen may pass through this thin layer and reach the zero moisture content region as shown in Fig. 1. Rate of passing may obviously be controlled by the diffusivity of this region having an equilibrium moisture content at a relative humidity h . Thus, it is shown that the equation (3) involves information of the equilibrium moisture content that cannot be obtained without waiting the infinite lapse of time.

The curve fitting program requires approximate coefficient values, as initial ones, to get optimum values after iterative calculations: an approximate convergence value of an adsorption for the parameter a , $6/\pi^2$ for b and 10^{-3} for c .

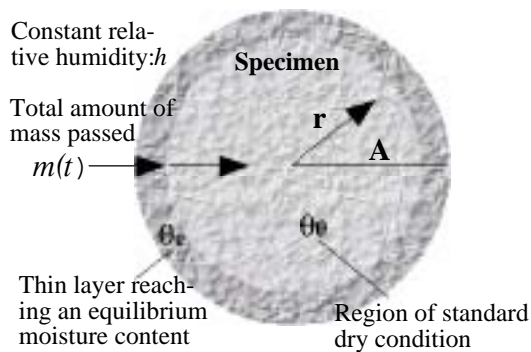


Fig. 1 Water vapor and HCP adsorption system

Table 1 Specimens and standard drying conditions

Type and dimensions (mm)	Bulk density (kg/m ³)	Manufacturing conditions	Standard drying conditions
HCP 100x100x10 shaped in diameter 10-15	2200 2100 1800	W/C=0.3 W/C=0.4 W/C=0.5 Cured in water	Under 20°C dry air with a dew point temp. of -42°C until equilibrium
ALC 100x100x30 shaped in diameter 10-15	480	Compatible to JIS A 5410 Autoclaved curing	Under 105°C forced electric oven until equilib- rium

3. Experiments

3.1 Specimens

Ordinary portland cement was mixed with water at a water-cement ratio of 0.3, 0.4 and 0.5, and molded in an acrylic form, a dimension of 100 x 100 x 10 mm, without remover chemicals. Specimens were demolded in the next day and cured under water for 8 weeks. Aerated concrete was a commercial product in accordance with Japanese Industrial Standards with a cutout dimension of 100 x 100 x 30 mm. These specimens were crushed with a hammer into pieces that all passed the 15 mm sieve and remained on the 10 mm sieve. Shape of the specimen may preferably be spherical as far as the equation (3) is applied, but polyhedral shape was used aiming at a simpler test method. A 10 to 30 grams of specimen was in a stainless steel basket hanging from the bottom hook of the electronic balance and exposed to a relative humidity in the specimen chamber of the humidity generator.

As the standard dry conditions, the D-dry method and 105 °C oven-dry method are normally used for hardened cement paste and aerated concrete. In this study, however, a method drying a specimen in the specimen chamber at the same temperature as that of subsequent adsorption was used. Dry-air of a dew point temperature of -42 °C was continuously supplied for 20 liters per minute. This method is milder than D-dry method that uses a dry-air of a dewpoint temperature of -76 °C but can dry specimens to a level closed to that of 105 °C oven-dry method. Furthermore, the drying is executed in the specimen chamber of the humidity generator, making it possible to proceed the subsequent adsorption experiment in a continuous manner. The standard drying conditions are shown in Table 1 together with the manufacturing conditions of the specimen.

3.2 Test apparatus

The test apparatus comprised three sets of a flow-division humidity generator and an electronic balance for mass determination, and all the balances were automatically controlled by a notebook computer. The configuration of the apparatus and the photo are shown in Fig. 2 and Fig.3.

The flow-division humidity generator can produce a relative humidity, flowing 20 liters per minute, at a precision of ± 1 percent or higher in a range from 0 to 95 percent. The nominal 0

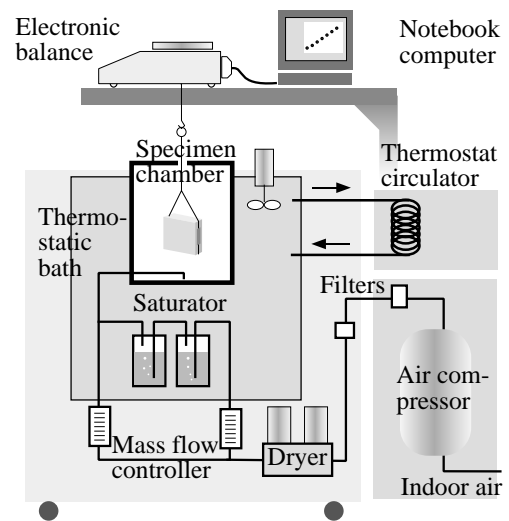


Fig. 2 System of the sorption isotherm apparatus



Fig. 3 Automatic testing apparatus

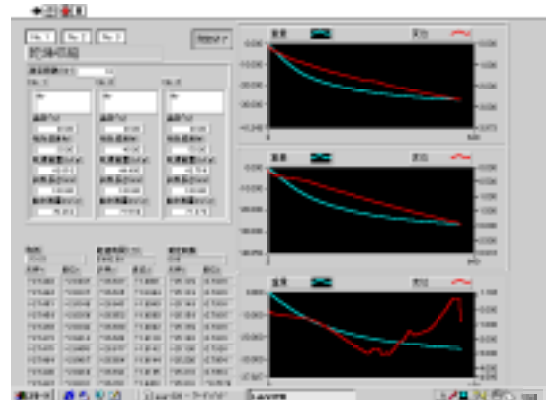


Fig. 4 Data acquisition program

percent relative humidity is a dry air having a dew point temperature of -42°C that correspond to a relative humidity of 0.27 percent at a room temperature of 20°C . The specimen chamber is shaped cylindrical, 200 mm in diameter and 250 mm in depth, and controlled at a constant temperature with a precision of ± 0.5 percent in a thermostatic water bath. The resolution of the electronic balance is 1 mg at the maximum weighing of 310 g. Three electronic balances are supported by each holder independent from the humidity generators and controlled by a notebook computer.

3.3 Automatic Measurement software

Automatic measurement program controls 6 RS-232C interfaced instruments, including 3 electronic balances, via an RS-232C multiplexer. User can start a measurement by interactively entering specimen conditions and measuring conditions from the screen. Results can be either monitored on the screen as a trend chart and saved as a tab-delimited ASCII file. Execution screen shots of the automatic measurement program is shown in Fig. 4 .

4. Results and discussion

4.1 Test results

(1) Aerated concrete

Specimens were kept in the standard dry condition of the specimen chamber, where each specified relative humidity of 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 95 percent was introduced subsequently resulting in adsorption of water into specimens. Changes in mass with changes in relative humidity are shown in Fig. 5. Each relative humidity corresponds to a curve consisting of 480 data points, once a minute for 8 hours. Equations (4a) and (4b) were used for curve fitting to the data and equilibrium moisture contents were determined. The resulting sorption isotherms are shown in Fig. 6. In each equation and for all curves, correlation coefficients of the curve fitting were greater than 0.994. In the mid range relative

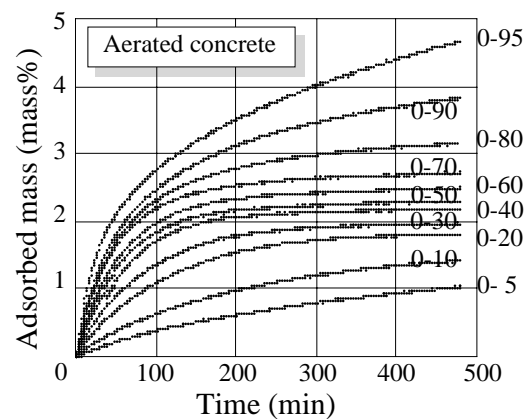


Fig. 5 Adsorption rate at various relative humidity changes

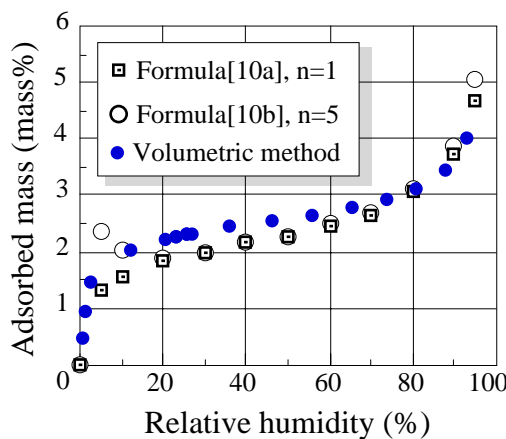


Fig. 6 Sorption isotherms of aerated concrete

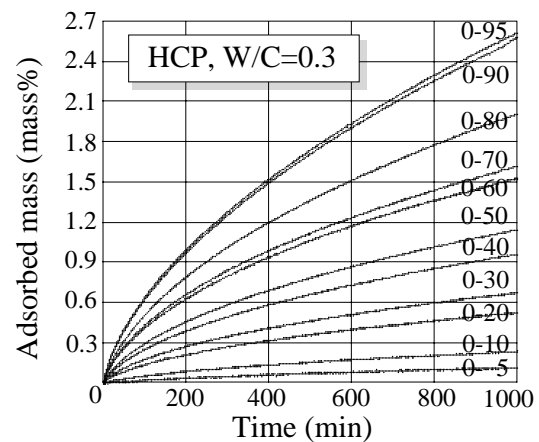


Fig. 7 Adsorption rate at various relative humidity changes

humidities, the equilibrium moisture content predicted by equations 4(a) and 4(b) were nearly identical, but differed in low and high humidity ranges. Especially in the low humidity range, equilibrium moisture content values predicted by equation 4(b) became very unusual. The volumetric method using a commercial equipment was applied to aerated concrete of the same brand. Result showed 0.3 percent higher than predicted values using equation (4) except for a high humidity range. This may be attributed to a large porosity of aerated concrete, more than 80 percent, where adsorption proceeded in a short time and reach the final stage of adsorption in 8 hours.

(2) Cement pastes

Experimental conditions were the same as those of the aerated concrete, and 11 different relative humidities were applied to cement pastes with water-cement ratio of 0.3, 0.4 and 0.5. Increase in adsorbed mass with changes in relative humidities is shown in Fig. 7. A curve consists of 1000 points corresponding to a measurement once a minute lasted for 17 hours. These data were subjected to the curve fitting of equation (4b) and the predicted equilibrium moisture contents are arranged in a sorption isotherm as shown in Fig. 8. Cement paste with a water cement ratio of 0.4 showed unexpectedly small value at a relative humidity of 95 percent, but the reinvestigation showed still the same result. A sorption isotherm of powdered cement paste with a water-cement ratio of 0.3 was determined by Yuasa and others using the saturated salt solution, which showed good agreement with this study as shown in Fig. 9. In the case of cement paste, with low porosity and hence taking longer time to reach an equilibrium, the equation (4) that is applicable to an early stage of adsorption may lead to a good result.

(3) Mortar

Mortar specimen was not prepared in this study but its sorption isotherm was calculated on the basis of the sorption isotherm of cement paste and the cement-sand ratio. A result of a specimen with water-cement ratio of 0.5 and sand-water ratio of 1:3 is

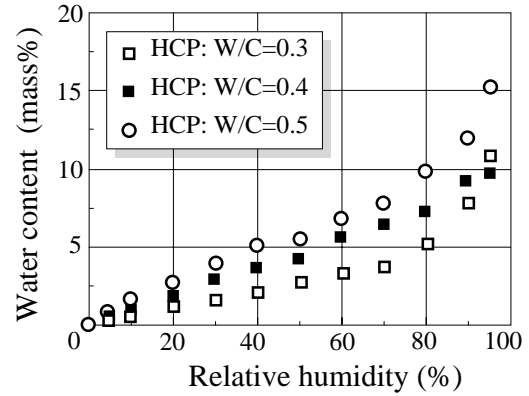


Fig. 8 Adsorption isotherms of hardened cement pastes

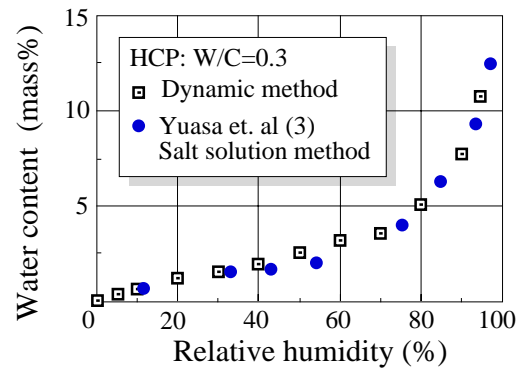


Fig. 9 Comparison of estimated isotherms of HCP with a literature value

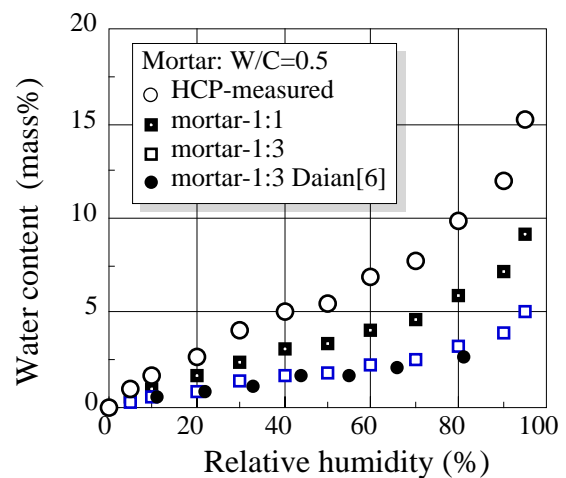


Fig. 10 Comparison of estimated isotherms of mortar with a literature value

shown in Fig. 10, where an experimental value of mortar of the same mix proportion determined by Daian [6], with the saturated salt solution method, is also given showing good agreement with our experimental value.

4.2 Possible causes of error

Among possible causes of the error in this dynamic method, nonfulfillment of the assumptions in the basic equation such as the shape of specimen may be included. Because the specimen was not a perfect sphere, the shape factor b in the curve fitting equation was not treated as a constant of $6/\pi^2$, but determined as a variable like a and c , resulting in the high correlation coefficient for all the adsorption data.

Application of curve fitting equations (4a) or (4b) corresponding to the stage of adsorption depends on the amount of specimen and the extent of the stepwise change of relative humidity, and cannot be determined uniformly. Measuring time, measurement interval and the limitation of applicability of the curve fitting equations were studied in a preliminary experiment using aerated concrete. Long term adsorption experiments were executed with measuring intervals of 10 seconds, 1 minute and 10 minutes and data was collected until the latter stage of adsorption as apparently observed in the adsorption curves. The results were verified by the correlation coefficients and the compatibility to literature values. As a result, it was decided that measuring interval was 1 minute and the measuring time was 8 hours for aerated concrete and 24 hours for hardened cement pastes.

Changes in performance of the testing apparatus with time may become a cause of error. Degradation of mass flow controller due to fine particles or oil mist and resulting decrease in accuracy of relative humidity generation may occur within several years. Changes in atmospheric pressure, when a moving low pressure approaches, may require corrections of the flow division table.

5 Conclusions

Water vapor adsorption rate of porous materials involves information of the equilibrium moisture content. Isothermal linear balance equation was solved in terms of the total moisture gain and this analytical form was used as a curve fitting scheme to the adsorption rate resulting in the early-stage prediction of the equilibrium moisture content. Results showed good agreement with those measured by the conventional methods. The adsorption rate experiment is simple and the time necessary for the prediction of an equilibrium moisture content in a relative humidity was 8 hours for aerated concretes and 12 hours for cement pastes.

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