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Dynamic determination of sorption isotherm of cement based materials

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Abstract

A dynamic method of determining sorption isotherm is proposed. Changes in humidity boundary conditions were applied to specimens of hardened cement paste having various water–cement ratios, as well as to autoclaved aerated concrete, and water adsorption rates were continuously recorded in a sufficiently short period. The diffusion equation was analytically solved and was fitted to the adsorption rates resulting in the rapid estimation of equilibrium moisture content. Results of equilibrium moisture content, the primary data of moisture capacity, showed good agreement with literature values. The adsorption rate measurement took 8 h for autoclaved aerated concrete and 12 h for hardened cement paste with a measurement interval of 60 s to predict an equilibrium moisture content at an ambient relative humidity.

Keywords: A: Humidity; C: Adsorption; C: Diffusion; D: Cement paste; Sorption isotherm

1. Introduction

Relationship between concentrations of a mass in a porous material isothermally in equilibrium with those 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 parameter when analyzing moisture behavior of cement based materials [1]. Especially in moisture transport analysis, moisture capacity that can convert the chemical potential gradient or relative humidity gradient into moisture content gradient, can be directly obtained from the water vapor sorption isotherm. As the name implies, it takes a long time to obtain real equilibrium values that difficulties of changes in material properties with hydration and subsequent carbonation 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, and an autoclaved aerated concrete, AAC. Stepwise changes in relative humidity were applied to the specimen and the adsorption rate was 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 equilibrium moisture content at a relative humidity.

2. Principle of measuring method

2.1. Conventional methods

Correct equilibrium moisture content can be obtained when relative humidities are accurately generated and 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 in a closed chamber. The volumetric method that

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isothermally changes the vapor pressure in a vacuum system has been widely used in chemical engineering laboratories.

The saturated salt solution method can produce a relative humidity with a precision of ±1% when the container of salt solution is stirred and the temperature is controlled carefully [2]. Haggymassy [3] used a weighing bottle with saturated salt solutions under vacuum and determined isotherms of hardened cement pastes. The mean free path of water vapor decreases under a reduced pressure leading to an increase in diffusivity of water vapor in air. This reduces the time to reach an equilibrium and is effective in preventing carbonation of cement based specimens. Yuasa and co-workers [4] ground specimens into a powder and introduced stirring mechanism in a saturated salt solution container. However, the saturated salt solution method has a disadvantage of generating a 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 flow-division humidity generator [5]. 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%–2% when employing the approximated formula specified in Japanese Industrial Standard-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 ±1%, 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, after the long period of adsorption rate monitoring, we 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 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 is given by

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

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 null,

$$\begin{aligned} &u = 0, r = 0, t \geq 0, \\ &u = R\theta_0, r = R, t > 0, \\ &u = 0, 0 < r < R, t = 0. \end{aligned} \tag{2}$$

With variables separation method, the following formula is obtained [6],

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

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 $D_\theta \pi^2/R^2$.

These initial and boundary conditions can be attained by providing the following experimental conditions: the specimen is kept under a 0% 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 Eq. (3), an $n=5$ polynomial may be a good approximation at an early stage of adsorption while $n=1$ may be a good approximation at all the stages, including the latter stage of adsorption. Thus executing the adsorption experiment of a spherical specimen and determining a, b and c in the following equation by non-linear curve fitting at a sufficiently high correlation factor, it is possible to predict the equilibrium moisture content θ_e by dividing a, corresponding to m_e in Eq. (3), with the standard dry mass.

$$m(t) = a[1 - b\exp(-ct)] \tag{4a}$$

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

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 null relative humidity for a sufficiently long time resulting in having uniformly null 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

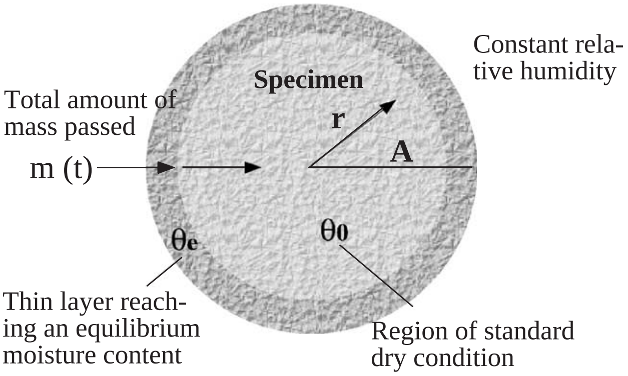


Fig. 1. Water vapor adsorption system in an HCP particle.

moisture entering in the specimen has to pass through this thin layer and reach the null moisture content region as shown in Fig. 1. Rate of moisture transport is obviously controlled by the diffusivity of this region with an equilibrium moisture content for a relative humidity h. Thus, it is shown that Eq. (3) involves information of the equilibrium moisture content that cannot be obtained without waiting for 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.

3. Experiments

3.1. Specimens

Ordinary portland cement compatible to the Japanese Industrial Standards JIS R 5210 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 × 100 × 10 mm, without a remover chemical. Specimens were demolded in the next day and cured in water-filled small plastic bags for 8 weeks. Autoclaved aerated concrete was a commercial product compatible to the Japanese Industrial Standards JIS A 5416 with a cutout dimension of 100 × 100 × 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 Eq. (3) is applied, but polyhedral shape was used aiming at a simpler specimen preparation. A 10–30 g of specimen was in a stainless steel basket hanging from the bottom hock of the electronic balance and exposed to a relative humidity in the specimen chamber of the humidity generator.

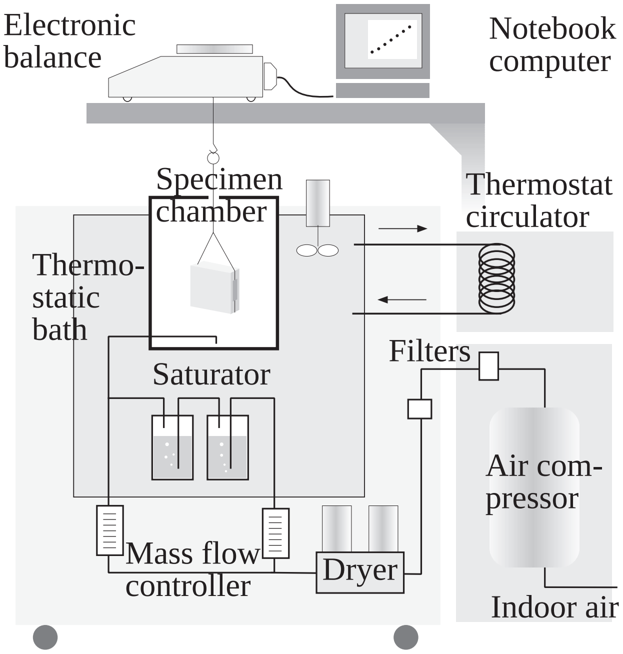


Fig. 2. System of the sorption isotherm apparatus.

As the standard dry conditions, the D-dry method and 105 °C oven-dry method are normally used for hardened cement paste and autoclaved 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 20 l per min. This drying method is milder than the D-dry method that uses a dry-air of a dew-point temperature of −76 °C but can dry specimens under room temperatures to a level closed to that of 105 °C oven-dry method. Furthermore, drying executed in the specimen chamber of the humidity generator makes 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 balance was automatically

Table 1
Specimens and standard drying conditions

Type and dimensions (mm)	Bulk density (kg/m^3)	Manufacturing conditions	Standard drying conditions
HCP 100 × 100 × 10 shaped in a of 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 100 × 100 × 30 shaped in a of diameter 10–15	480	Compatible to JISA 5410 Autoclave curing	Under 105 °C forced electric oven until equilibrium

Fig. 3. Automatic testing apparatus.

controlled by a notebook computer. The configuration of the apparatus and the photo are shown in Figs. 2 and 3.

The flow-division humidity generator, flowing 20 l per min, can produce a relative humidity at a precision of ±1% or higher in a relative humidity range from 0 to 95 %. The nominal 0 % relative humidity is a dry air having a dew-point temperature of −42 °C that corresponds to a relative humidity of 0.27 % at a room temperature of 20 °C. Because the dry air was generated with molecular sieve 5A dryer, atmospheric carbon dioxide can be removed to a level free from carbonation during adsorption experiment. The specimen chamber was shaped cylindrical, 200 mm in diameter and 250 mm in depth, and controlled at a constant temperature with a precision of ±0.5 °C in a thermostatic water bath. The resolution of the electronic balance was 1 mg at the maximum weighing of 310 g. Three electronic balances were supported with each holder independent from the humidity generators.

3.3. Automatic measurement software

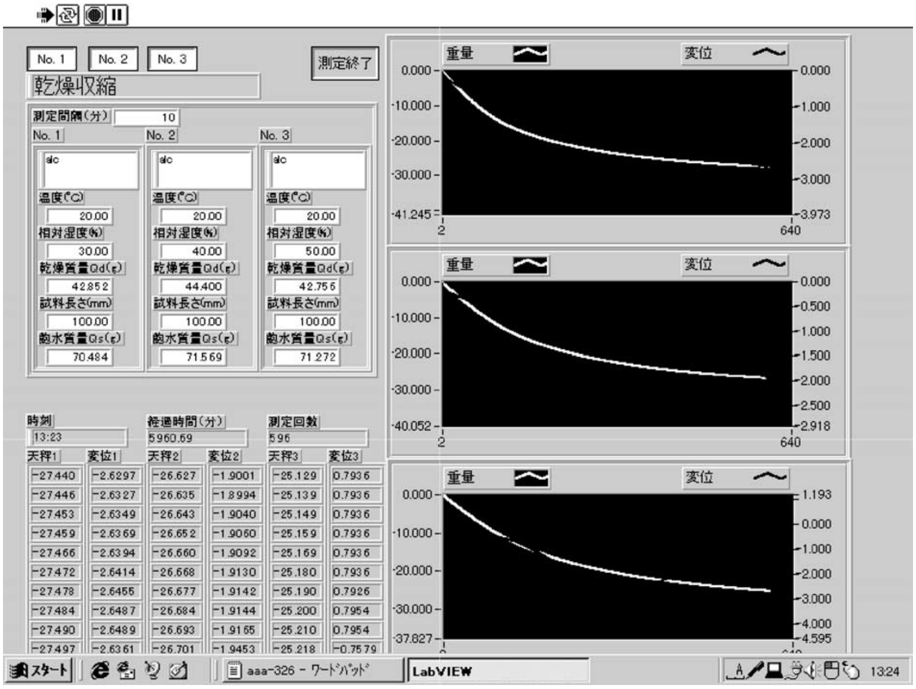
Automatic measurement program controls six RS-232C interfaced instruments, including 3 electronic balances, via an RS-232C multiplexer. User can start a measurement by interactively entering specimen conditions and measuring conditions from the screen. Results can be monitored on the screen as a trend chart and saved as a tab-delimited ASCII file. The file names can be automatically generated, where it is possible for one to know the date, number of measurement of the day, identifier of equipment used and type of measurement by the generated file name alone. Execution screen shot of the automatic measurement software is shown in Fig. 4.

4. Results and discussion

4.1. Test results

4.1.1. Autoclaved 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 % 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 h.



乾燥収縮

測定間隔(分) 10

No. 1
alc
温度(℃) 20.00
相対湿度(%) 30.00
乾燥質量Qd(g) 42.852
試料長さ(mm) 100.00
飽水質量Qs(g) 70.484

No. 2
alc
温度(℃) 20.00
相対湿度(%) 40.00
乾燥質量Qd(g) 44.400
試料長さ(mm) 100.00
飽水質量Qs(g) 71.569

No. 3
alc
温度(℃) 20.00
相対湿度(%) 50.00
乾燥質量Qd(g) 42.756
試料長さ(mm) 100.00
飽水質量Qs(g) 71.272

時刻 13:23
経過時間(分) 5960.69
測定回数 596

天秤1	変位1	天秤2	変位2	天秤3	変位3
-27.440	-2.6297	-26.627	-1.9001	-25.129	0.7936
-27.446	-2.6327	-26.635	-1.8994	-25.139	0.7936
-27.453	-2.6349	-26.643	-1.9040	-25.149	0.7936
-27.459	-2.6369	-26.652	-1.9060	-25.159	0.7936
-27.466	-2.6394	-26.660	-1.9092	-25.169	0.7936
-27.472	-2.6414	-26.668	-1.9130	-25.180	0.7936
-27.478	-2.6455	-26.677	-1.9142	-25.190	0.7926
-27.484	-2.6487	-26.684	-1.9144	-25.200	0.7954
-27.490	-2.6489	-26.693	-1.9165	-25.210	0.7954
-27.497	-2.6361	-26.701	-1.9453	-25.218	-0.7579

Fig. 4. Data acquisition software.

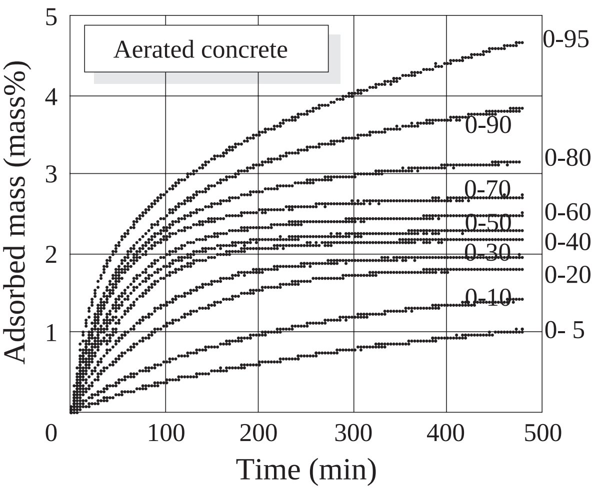


Fig. 5. Absorption rate at various relative humidity changes.

Eqs. (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 humidities, the equilibrium moisture content predicted with Eqs. (4a) and (4b) were nearly identical, but differed in low and high humidity ranges. Especially in the low humidity range, equilibrium moisture content values predicted by Eq. (4b) became very unusual. Thus the Eq. (4a) was employed throughout the subsequent experiments.

The volumetric method using a commercial instrument was applied to autoclaved aerated concrete of the same brand. The result showed 0.3 % higher equilibrium moisture content than that predicted using Eqs. (4a) and (4b) except for a high humidity range. This may be attributed to a large porosity of autoclaved aerated concrete, more than 80 %, where adsorption proceeded in a short time and reached the final stage of adsorption in 8 h resulting in violating the principle of the dynamic method that the thin surface layer controls the net moisture flow only at an early stage of adsorption.

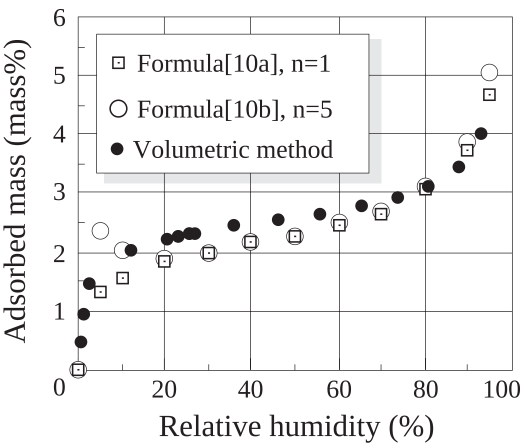


Fig. 6. Sorption isotherms of aerated concrete.

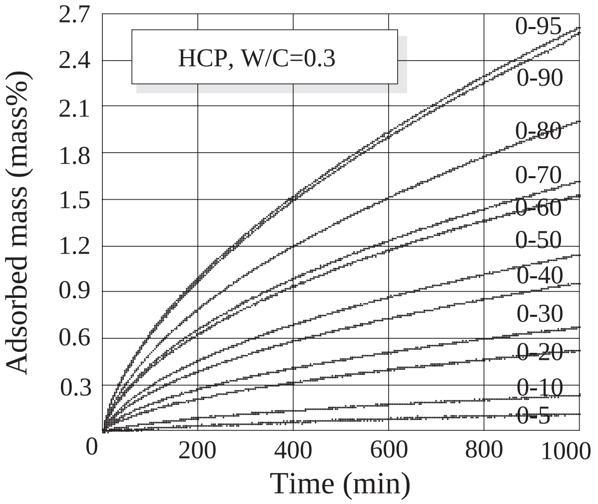


Fig. 7. Adsorption rate at various relative humidity changes.

4.1.2. Cement pastes

Experimental conditions were the same as those of the autoclaved 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 h. These data were subjected to the curve fitting of Eq. (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 an unexpectedly small value at a relative humidity of 95 %, 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 equilibrium, the Eqs. (4a) and (4b) that are applicable to an early stage of adsorption may lead to a good result.

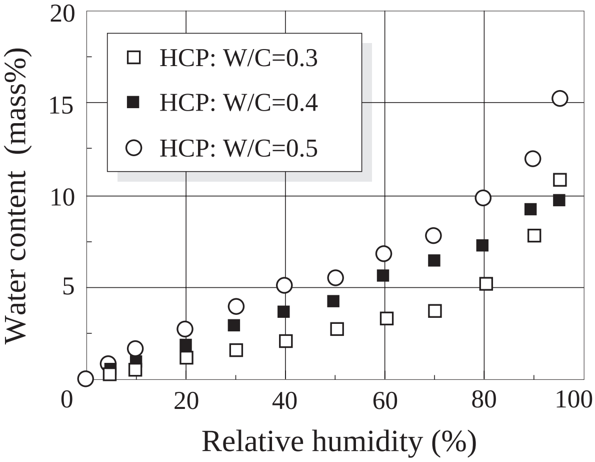


Fig. 8. Adsorption isotherms of hardened cement pastes.

4.1.3. 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 cement–sand ratio of 1:3 is shown in Fig. 10, where an experimental value of mortar of the same mix proportion determined by Daian [7] with the saturated salt solution method is also given showing good agreement with those of the dynamic method.

4.2. Possible causes of error

4.2.1. Assumption in the basic equation

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.

4.2.2. Experimental conditions

Application of curve fitting Eqs. (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 duration, measurement interval and the limitation of the curve fitting equations were studied in a preliminary experiment using autoclaved aerated concrete. Long term adsorption experiments were executed with measuring intervals of 10 s, 1 min and 10 min and data was collected until the latter stage of adsorption as apparently shown from 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 min and the measuring time was 8 h for autoclaved aerated concrete and 24 h for hardened cement pastes.

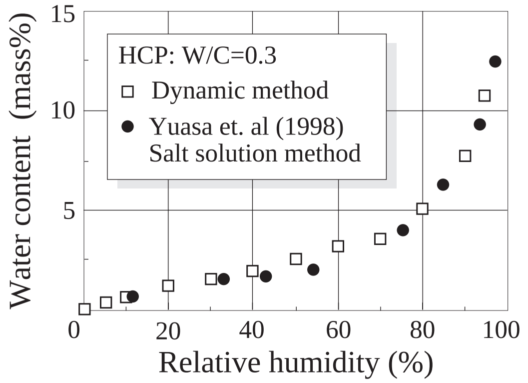


Fig. 9. Comparison of estimated isotherms of HCP with a literature value.

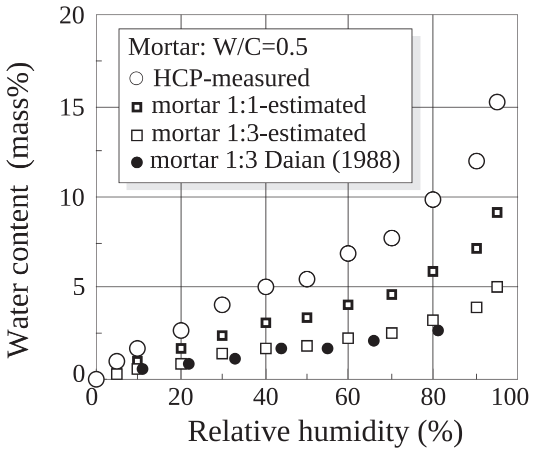


Fig. 10. Comparison of estimated isotherms of mortar with a literature value.

4.2.3. Conditions of test apparatus and specimen

Changes in performance of the testing apparatus with time may also 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 the atmospheric pressure, when a moving low pressure approaches for instance, may require corrections of the flow division table. Electronic balance may show a shift when an abnormal acceleration is applied by, for instance, earthquakes. It is also affected by the thermal drift and air current in the thermostatic chamber.

Lack of knowledge about the nature of specimen may lead to an error. When a cement-based material is subjected to change in pore structure during testing by for instance hydration or carbonation, the sorption isotherm changes to a great extent. Drying under a room temperature is preferable to have a standard drying condition regardless of the type of specimen, and the dryness of the conditioned air should be defined in terms of a dew-point temperature. Autoclaved aerated concrete can be dried at an oven-dry temperature of 105 °C, but the long term drying may dehydrate the surface silanol group and revive the siloxane bonds resulting in the hydrophobic surface. Prior to the experiment, autoclaved aerated concrete was kept under 0% relative humidity for one day. Such drying conditions have not been well documented making it difficult to compare with the literature values.

5. Conclusions

Rate of water adsorption to cement paste 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 obtaining an equilibrium moisture content in a relative humidity was 8 h for aerated concretes and 12 h for cement pastes. Departing from the accepted notion, the information of equilibrium moisture content hidden in an adsorption rate is best manifested even at an adsorption stage very far from the equilibrium.

This method has been further extended to determine both equilibrium moisture content and moisture diffusivity of porous materials simultaneously [8].

References

[1] K. Maekawa, T. Ishida, T. Kishi, Multi-scale modeling of concrete performance—integrated material and structural mechanics, Journal of Advanced Concrete Technology 1 (2) (2003) 91–126.

[2] H. Kitano, C. Takahashi, T. Inamatsu, Standard humidities generation by saturated salt solutions, Transactions of SICE 23 (12) (1987) 1246–1253 (in Japanese).

[3] J. Haggymassy Jr., Pore structure analysis by water vapor adsorption, Ph.D. Thesis. Department of Chemistry, Clarkson College of Technology, 1970.

[4] N. Yuasa, et al., Sorption isotherm and moisture conductivity of cover concrete, Cement Science and Concrete Technology 52 (1998) 1042–1049 (in Japanese).

[5] C. Takahashi, T. Inamatsu, H. Kitano, Construction of flow-division humidity generator, Transactions of SICE 24 (6) (1988) 557–562 (in Japanese).

[6] J. Crank, The Mathematics of Diffusion, 2nd ed., Oxford Science Publications, 1975.

[7] J.-F. Daian, Condensation and isothermal water transfer in cement mortar, Transport in Porous Media 3 (1988) 563–589.

[8] S. Tada, K. Watanabe, Simultaneous determination of moisture capacity and water diffusivity of cement based materials, Cement Science and Concrete Technology 55 (2002) 54–61 (in Japanese).