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論文 Modeling of Pore Water Content in Concrete under Generic Drying Wetting Conditions

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ABSTRACT: In this paper, we propose an analytical model to represent the hysteresis behavior of moisture isotherm of concrete. Microstructure of concrete is approximated by a porosity distribution to which proposed analytical model is applied to predict the concrete water content under variable environmental conditions. The proposed model is based upon the physical phenomenon called the inkbottle effect in porous medium. The proposed model can predict the water content in concrete under general drying-wetting conditions satisfactorily.

KEYWORDS: Durability, Pore structure, Isotherm, Hysteresis, Inkbottle-effect.

1. INTRODUCTION

Most of the deterioration mechanisms of concrete structure, such as cracking due to drying shrinkage, carbonation, corrosion and sulfate attack etc. are related to the water content in concrete. It is therefore indispensable to predict the water content in concrete under any environmental conditions for a rational and quantitative durability design of the concrete structures.

Cement paste is a porous media which has various sizes and configurations of pores, and moisture in these pores can be present in both liquid and vapor form. Usually, the volumetric content and thermodynamic characteristics of these two phases of moisture dispersed in capillary and gel pores are determined by the Kelvin's equation which expresses the thermodynamic equilibrium between liquid water and vapor. In this approach, the equilibrium is assumed to be perfectly reversible under various environmental conditions, such as drying and wetting stages. However, it is experimentally known that the water content in concrete is different under drying and wetting stages, even if exposed to the same relative humidity. This phenomena is called hysteresis and can be explained by various mechanisms, such as inkbottle effect, irreversibility of adsorption and desorption of water molecule to micropore structures etc. However, a rational and quantitative method to express this irreversible hysteresis phenomena for practical evaluations of moisture content in a porous body does not exist. Therefore, in this paper, we attempt to model the path-dependence of water content in concrete on arbitrary drying-wetting conditions, considering mainly inkbottle effect.

2. COMPUTATIONAL MODEL OF ISOTHERM

Ideally, for a typical moisture isotherm, absorption and desorption curves are expected to be similar. In actual cases however, a different behavior for these curves can be observed in not only concrete, but also other porous medium. Irreversibility of water content in concrete under cyclic

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drying-wetting condition is shown in Fig.1 [1]. All desorption curves lie above the adsorption curves and hysteresis loops can be observed. To predict such behavior, we define a porosity distribution function [2,3] of cement paste and propose a generic model of moisture isotherm considering thermodynamic equilibrium of phases and the inkbottle effect.

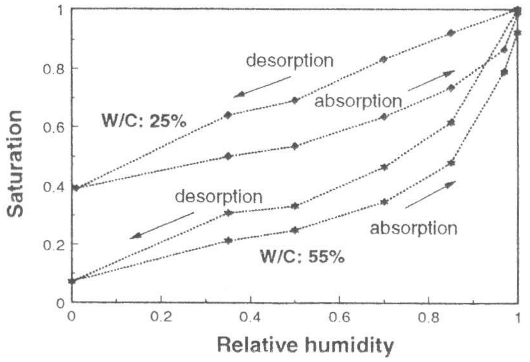

Fig 1 : Absorption and desorption isotherms [1]

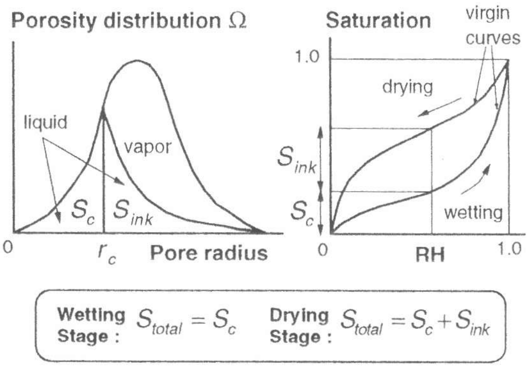

Fig 2 : Moisture distribution in porestructure under drying wetting conditions.

2.1 POROSITY FUNCTION OF CEMENT PASTE

There are various sizes of pores in actual concrete. In this paper, we consider only those pores that influences moisture transport in concrete. These pores are classified into capillary, gel and interlayer pores. The total porosity distribution function is obtained by considering a coupled hydration, moisture transport and porestructure formation models as [3]

$$\phi(r)=\phi_l+\phi_g\left\{1-\exp\left(-B_g r\right)\right\}+\phi_c\left\{1-\exp\left(-B_c r\right)\right\} \tag{1}$$

where r : pore radius, ϕ_l : interlayer porosity, ϕ_g : gel porosity, ϕ_c : capillary porosity, B_g : gel porosity distribution parameter, B_c : capillary porosity distribution parameter. For the sake of simplicity, we will consider a unimodal pore distribution given as V=1-exp(-Br) in subsequent sections.

2.2 COMPUTATIONAL MODEL OF HYSTERETIC BEHAVIOR OF ISOTHERM

2.2.1 Inkbottle models of capillary and gel pores (primary loops)

Under equilibrium conditions moisture content of a porous media is dependent on the ambient relative humidity. This is because, for a given relative humidity, certain group of pores whose radii is smaller than the pore radius in which liquid-vapor interface is formed are completely filled with water, whereas larger pores remain empty or partially saturated. Considering local thermodynamic and interface equilibrium in a porous media, the radius r_s of the pore in which the interface of liquid and vapor is created can be determined by the Kelvin's equation as [2],

$$\ln\left(\frac{P_v}{P_{vO}}\right)=-\frac{2\gamma M}{RT\rho_L}\frac{1}{r_s} \tag{2}$$

where P_v/P_{v0} : relative humidity of vapor phase, γ : surface tension of liquid water (N/m), M: molecular mass of water (kg/mol), R : universal gas constant (J/mol.K), T : absolute temperature of the vapor liquid system (K), ρ_L : density of liquid water (kg/m^3). In the past, above assumption was usually applied for the prediction of moisture state in concrete [2]. However, eq. 2 is not adequate enough to describe the moisture state in concrete, since it can not explain the adsorption of water molecules in micropores. Moreover, it fails to address the hysteresis behavior. In this paper, we consider both the condensed and adsorbed phases of liquid water. Consideration of adsorption using a modified BET model [4] implies that the equilibrated interface of liquid and vapor is created in a pore of radius r_c, which is larger than the pore radius r_s as determined by eq. 2. In other words, pores of radii smaller than r_c are completely saturated, whereas larger pores are partially or completely saturated depending on the drying wetting history. Also, an adsorbed film of thickness of few water molecules exists in the unsaturated pores. For the sake of simplicity, the adsorbed component of moisture is neglected from the following derivations as this component can be simply added to the results obtained in this paper, thereby giving total saturation.

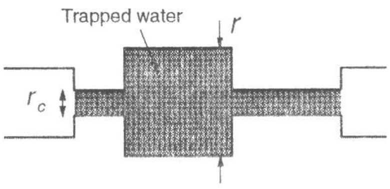

Fig 3 : Inkbottle effect in an idealized pore.

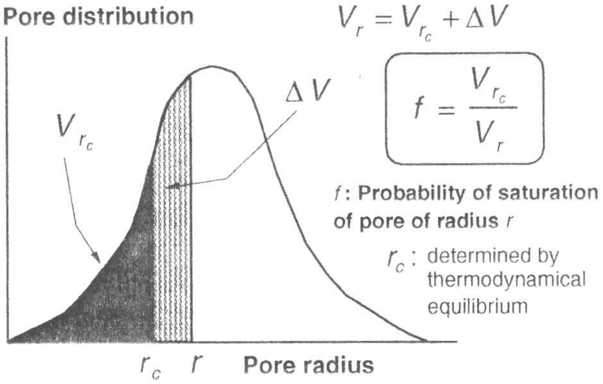

Fig 4 : Definition of the hysteresis model

(a) Wetting stage :

First of all, we consider virgin wetting curve, where absorption starts from a completely dried state of the porous media. At any location under equilibrium conditions, the pores whose radii are smaller than r_c would be completely saturated [2], whereas larger pores would only contain moisture in the adsorbed phase, which is neglected here for the sake of brevity. Therefore, total saturation S_{total} of the pore distribution can be obtained by integrating the individual micropore saturation over entire porosity distribution function as (Fig.2),

$$S_{total} = S_c = \int_0^{r_c} \Omega dr = \int_0^{r_c} dV = 1 - \exp(-Br_c) \tag{3}$$

where $V = 1\text{-}\exp(\text{-}Br)$ is the normalized volumetric porosity function, $1\text{-}\exp(\text{-}Br)$ and $\Omega = dV/dr$ is the porosity distribution function. In other words, total saturation in this case is obtained by simply adding up the condensed pore volumes and does not includes any contribution due to hysteresis.

(b) Drying stage :

As we have already mentioned, the virgin drying curve of moisture isotherm is always found to be higher than the corresponding wetting curve. To describe this behavior, we focus primarily on the inkbottle effect, which might be one of the main reasons of hysteresis. The inkbottle effect in an idealized pore can be shown as in Fig.3, which shows that during drying we can expect some additional trapped water in the pores whose radii r is larger than r_c. Such pores have external openings only through pores of smaller radii, and therefore cannot lose moisture as long as the connecting pores remain saturated. To consider the volume of entrapped water in such pores, we define a probability parameter f for hysteresis behavior taking into account the geometric characteristics of pores (Fig.4). The parameter f denotes the probability of water entrapment in a pore of radii r larger than the pores of radii r_c. In other words, this fraction is the probability that the pore of radius r would be connected only to the pores whose radius is smaller than r_c. Based on this discussion a mathematical definition of f can be given as,

$$f = \frac{V_{r_c}}{V_r} \tag{4}$$

where, V_{rc} : volume of the pores until radius r_c. V_r : volume of the pore until radius r. Using this assumption, the saturation owing to inkbottle effect S_{ink} can be obtained as,

$$S_{ink} = \sum_{r=r_c}^{\infty} f\,\Omega\Delta r = \int_{r_c}^{\infty} f\,dV = \int_{r_c}^{\infty}\left(\frac{S_c}{V}\right)dV = -S_c \ln(S_c) \tag{5}$$

Therefore, total saturation under virgin drying condition can be obtained as follows. (Fig.2)

$$S_{total} = S_c + S_{ink} = S_c\left[1 - \ln S_c\right] \tag{6}$$

It can be noticed, that the additional term $-S_c \ln S_c$ is always positive, which proves the observation that drying curves are always higher than the absorption curves. Also, it vanishes at unit saturation value, when both the drying and wetting curves meet.

2.2.2 Inkbottle models of capillary and gel pores (scanning curves)

In the previous section, a computational model was built for a quantitative representation of virgin wetting-drying behavior of moisture in concrete. However, actual concrete structures are often exposed to variable environmental conditions, which can not be predicted by only virgin loops. Therefore we need to extend the application of this concept besides virgin wetting-drying paths for arbitrary environmental conditions, such as complicated cyclic wetting-drying conditions. Similar to the virgin wetting and drying stages, we consider following two cases for discussion which cover all possible scenarios of drying wetting paths.

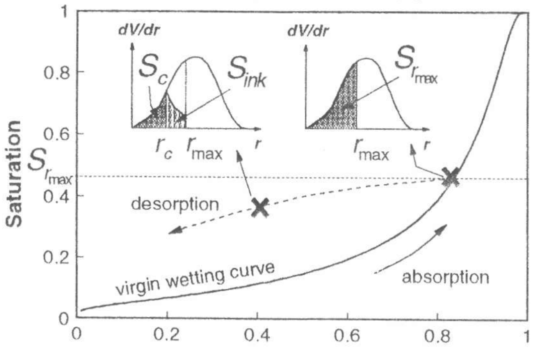

Fig 5 : An inner loop from wetting to drying stage

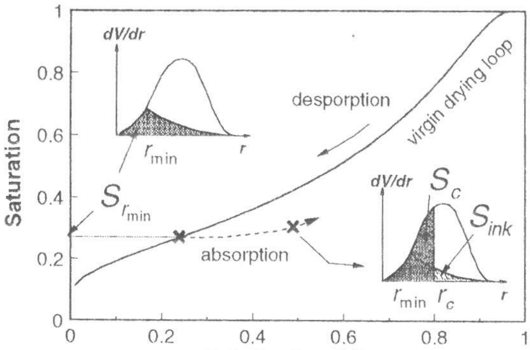

Fig 6 : An inner loop from drying to wetting stage

(c) From virgin wetting path to drying and subsequent loops :

During the monotonous wetting phase, absorption curve would be similar to the virgin wetting curve. However, when the relative humidity decreases, desorption curve is assumed not to return to the virgin curve, but instead trace an scanning drying curve as shown in Fig.5. For scanning drying curves, the inkbottle model is applied and the saturation owing to inkbottle effect S_{ink} can be given as,

$$S_{ink} = \int_{r_c}^{r_{max}} \frac{S_c}{V}\,dV = S_c\left[\ln S_{r_{max}} - \ln S_c\right] \tag{7}$$

where r_{max} : pore radius of the largest pores which experienced a complete saturation in the wetting history of the porous media, S_{rmax} : highest saturation experienced by the porous media in its wetting history. Thus, total saturation as a sum of the usual condensed and entrapped water is obtained as,

$$S_{total} = S_c + S_{ink} = S_c\left[1 + \ln S_{r_{max}} - \ln S_c\right] \tag{8}$$

In the inner loops, absorption and desorption processes are assumed to be reversible so that the inner scanning curves follow a similar path. Moreover, in the dry-wet history if wetting proceeds such that r_c exceeds r_{max}, adsorption path will return to the virgin wetting loop. We have assumed the reversibility of the inner loops primarily to obtain a closed form analytical solution of the hysteresis model. Of course, based on the ink-bottle concept discussed earlier, it is possible to trace exact hysteresis behavior in the inner loops. However, this would require keeping trace of all the turning points in drying wetting history and therefore, would limit the practical applicability of the model.

(d) From virgin drying path to wetting and subsequent loops :

Similar to the previous case, during first drying, saturation would decrease along the virgin drying loop. However, when the ambient relative humidity increases, scanning absorption loop would be formed and a gradual moisture re-entry from filling up of smaller pores would take place (Fig.6). For this case, total saturation which is the sum of S_c and S_{ink} can be obtained as,

$$S_{total} = S_c + S_{ink} = S_c + \int_{r_c}^{\infty} \left(\frac{S_{r_{min}}}{V} \right) dV = S_c - S_{r_{min}} \ln S_c \qquad (9)$$

where r_{min} : pore radius of the smallest pores which experienced an emptying out in the drying history S_{rmin} : lowest saturation of the porous media in its wet-dry history. The scanning curves of absorption and desorption paths are assumed to be similar owing to the reasons explained earlier. As drying proceeds such that r_c becomes smaller than r_{min}, desorption path will again return to the virgin drying loop. It must be noted, that in all of the above derivations we have neglected the adsorbed component of pore water which exists in the form of a film of thickness of few water molecules.

3. VERIFICATIONS

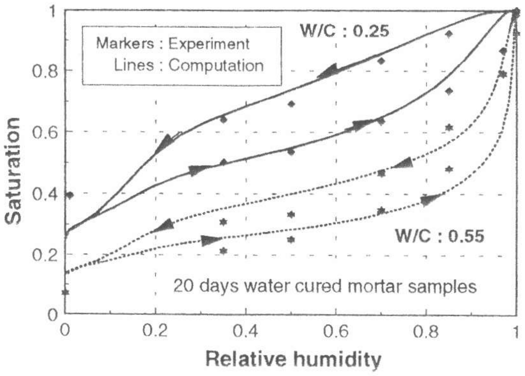

Fig 7 : Experimental and computed isotherms for different mortars (Table 1).

To verify the proposed hysteresis model, it was implemented as a part of the moisture transport model into a fintite-elment computational program DuCOM which can deal with the coupled pore-structure development, hydration and moisture transport behaviors of early aged concrete [3]. Using this program, we can obtain solutions of temperature, pore pressure, pore distributions and other material properties in 3-D space and time domain. The proposed model was verified by comparing the computed results to the experimental data of isotherms and moistre loss measurements of mortars exposed to a cyclic wetting drying boundary condition.

Table 1: *Mix proportions of mortar used in isotherm measurement experiment*

Mix No.	W/C (%)	Mix Unit Weight (kg/m^3) *W*	 *Sand*	 *Medium Heat Cement*
1	25	266	1036	1064
2	55	382	1036	694
3	25	289	917	1144

Fig.7 shows a comparison of computed and experimental isotherms. In the experiment, after 20 days of water curing, the mortar specimens were broken into several smaller pieces (about 1 cm^3 each) and kept in a humidity-temperature control chamber. The relative humidity inside the chamber was gradually decreased in several steps by keeping each step constant for more than two days. After that, the samples were freeze dried and again exposed to increasing humidity in several steps with each step held constant for about two days. Weight measurements were taken at the end of each step to obtain water-content and isotherm loops. Computed results shows that both the wetting and drying loops are well predicted for different water to powder ratio. In the FEM analysis, boundary condition for freeze drying was taken as 0.005 RH.

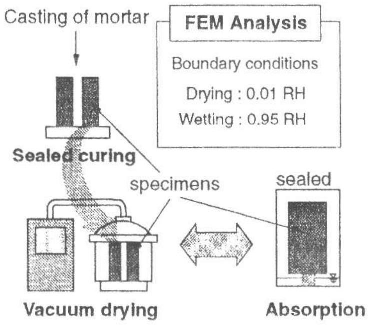

Fig 8a : Schematic representation of drying wetting experiments and computation scheme

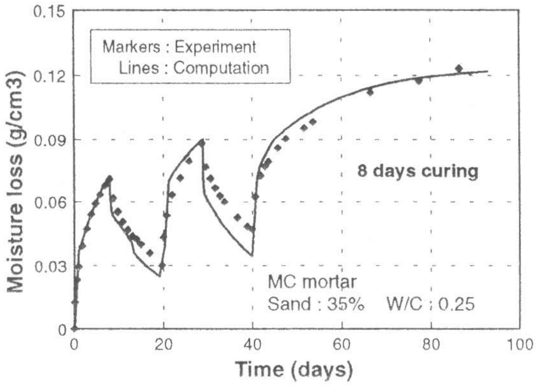

Fig 8b : A comparison of the computed and measured moisture loss data for cyclic dry-wet conditions

The second case is the prediction of weight loss behavior with time under cyclic drying wetting conditions. Experimental procedure, data[5] and a computed result are shown in Fig.8. We can find reasonable agreement not only in the rate of weight loss, but also in the absolute amount of weight loss. Without using hysteresis models, such an agreement, could not be obtained.

4. CONCLUSIONS

An analytical model to compute moisture isotherms of concrete considering the inkbottle effect is proposed. It seems that the model is applicable to cementitious microstructures, since it is based on the geometrical characteristics of random pore-structures. Using this model as a part of the moisture transport models, moisture condition of concrete for arbitrary ambient relative humidity can be predicted. The computed results show that the simulated isotherms and weight loss behavior of mortar under cyclic drying-wetting conditions have reasonable agreement with the experimental data.

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