

# Creep and Shrinkage of Concrete

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## 22 IMPROVED PORE WATER DIFFUSION MODEL FOR CREEP ANALYSIS OF CONCRETE STRUCTURES

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### Abstract

*As an improvement over a preceding diffusion equation model by Bažant and Najjar, the moisture capacity and diffusivity are treated as two separate coefficients. The moisture capacity is determined from the adsorption theory and is calibrated from adsorption isotherm measurements. The diffusivity is analyzed on the basis of diffusion mechanisms in concrete and is calibrated by diffusion test data. The effects of the water-cement ratio, curing time, cement type, and temperature are taken into account.*

**Keywords:** Concrete, Drying, Water Diffusion, Adsorption, Permeability, Diffusivity, Capillarity

### 1 Introduction

The properties of cementitious materials depend strongly on the moisture content. Therefore, knowledge of the evolution of moisture distributions within concrete structures is of considerable practical importance. This is especially true if time-dependent phenomena such as creep, shrinkage, fire resistance, and durability are analyzed. Analysis of moisture diffusion is an inevitable component of any serious study of shrinkage or drying creep. The migration of moisture within concrete can be expressed by the diffusion equation

$$\frac{\partial W}{\partial t} = \frac{\partial W}{\partial H} \frac{\partial H}{\partial t} = -\operatorname{div}(J) = \operatorname{div}(D_h \operatorname{grad} H) \quad (1)$$

in which  $t$  is time,  $W$  is water content,  $H$  is pore relative humidity,  $J$  is moisture flux, and  $D_h$  is humidity diffusivity. In Eq. 1, two coefficients must be determined: moisture capacity,  $\partial W/\partial H$ , and humidity diffusivity,  $D_h$  (which is proportional to permeability). Both coefficients depend on  $H$ , which causes nonlinearity of Eq. 1. The determination of these coefficients is more complex than in most other porous media because a very wide range of pore sizes occurs in cement paste, and also because the pore structure changes with age. Over the past several decades, a number of theoretical models have been proposed. However, a reliable and general theoretical model does not yet exist.

The main purpose of this study is to briefly outline an improvement of the existing model Bažant and Najjar, (1972) which will be given detail in Bažant, Xi and Molina (1993). First, a semi-empirical expression for the adsorption isotherm will be developed by parametric analysis of adsorption test data. The temperature effect will be included automatically. The diffusivities corresponding to various diffusion mechanisms, and the influences of various parameters will be analyzed, and the proposed formulation will be calibrated according to some recent diffusion test results.

## 2 Adsorption Isotherm

The moisture capacity is the derivative of the equilibrium adsorption isotherm. Therefore, the adsorption isotherm must be analyzed first. The most widely used isotherm model is the BET model (Brunauer, Emmett and Teller, 1938), derived from statistical thermodynamics of adsorption. But contrary to what was previously supposed, the range of validity of the BET equation for cement and concrete does not always extend over the ranges of relative pressure (humidity) from 0.05 to 0.30 or from 0.05 to 0.50, but sometimes only extends over the range from 0.01 to 0.1 (Gregg, et al., 1982; Mikhail, 1983). A number of attempts have been made to modify the BET equation in order to obtain better agreement with experimental isotherm data in the multilayer region. Among them, the BSB model (Brunauer, Skalny, and Boder, 1969) will be used in this study. This model is also called the three-parameter BET model, since it is a generalization of the BET model. The BSB model reads

$$W = \frac{CkV_m H}{(1 - kH)[1 + (C - 1)kH]}, \quad C = \exp\left(\frac{E_1 - E_l}{RT}\right) \quad (2)$$

where  $H = p/p_s$ ,  $V_m$  is the monolayer capacity,  $C = \text{constant}$ ;  $k = \text{coefficient}$  that must have a value of less than 1;  $p_s$  is the pressure at saturation;  $E_1$  is the total heat of adsorption per mole of vapor; and  $E_l$  is the molar heat of condensation;  $R$  is the gas constant;  $T$  is the absolute temperature, and  $W$  is the mean of vapor per unit mass of cement paste adsorbed at pressure  $p$  in g/g.

The adsorption of portland cement is influenced by many parameters. In general, those which affect the adsorption isotherm include any parameter that contributes to the hydration process of portland cement and hence to the constitution of the pore structure and the pore size distribution. In this study, only the effects of the original water-cement ratio  $w/c$ , age  $t$ , temperature  $T$ , and cement type are established in an empirical relationship with the amount of adsorption.

In Eq. 2, three parameters need to be determined; they are  $V_m$ ,  $C$ , and  $k$ .  $V_m$  is called monolayer capacity, and is defined as the quantity of adsorbate required to cover the adsorbent with a single molecular layer,  $C$  is related to the temperature, and  $k$  results from the assumption of the model that the number of adsorbed layers is finite, possibly even a small number. These three parameters have been determined by calibrations of the available adsorption test data. The procedure is given in detail elsewhere (Bažant, Xi, and Molina, 1993). The results are as follows:

$$V_m = \left(0.068 - \frac{0.22}{t_e}\right) \left(0.85 + 0.45\frac{w}{c}\right) V_{ct}, \quad t > 5 \text{ days, } 0.3 < w/c < 0.7 \quad (3)$$

but for  $t \leq 5$  days: set  $t = 5$  days; for  $w/c \leq 0.3$ : set  $w/c = 0.3$ ; for  $w/c \geq 0.7$ : set  $w/c = 0.7$ ;  $V_{ct}$  depends on type of cement—Type 1:  $V_{ct} = 0.9$ ; Type 2:  $V_{ct} = 1$ ; Type 3:  $V_{ct} = 0.85$ ; Type 4:  $V_{ct} = 0.6$ ;  $t_e$  is the equivalent curing period (maturity) (for room temperature,  $t_c = t$ );

$$C = \exp\left(\frac{C_0}{T}\right), \quad k = \frac{\left(1 - \frac{1}{n}\right)C - 1}{C - 1},$$

$$n = \left(2.5 + \frac{15}{t_e}\right) \left(0.33 + 2.2\frac{w}{c}\right) N_{ct}, \quad t > 5 \text{ days, and } 0.3 < w/c < 0.7 \quad (4)$$

but for  $t \leq 5$  days: set  $t = 5$  days; for  $w/c \leq 0.3$ : set  $w/c = 0.3$ ; for  $w/c \geq 0.7$ : set  $w/c = 0.7$ ;  $N_{ct}$  depends on the type of cement—Type 1:  $N = 1.1$ ; Type 2:  $N_{ct} = 1$ ; Type 3:  $N_{ct} = 1.15$ ; Type 4:  $N = 1.5$ ;  $C_0 = 855$ ;  $n$  in Eq. 4 is the number of adsorbed layers at saturation state. Certain microstructure features can be associated with the above equations, but cannot be described here.

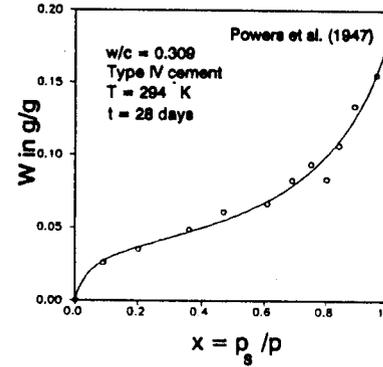


Fig. 1

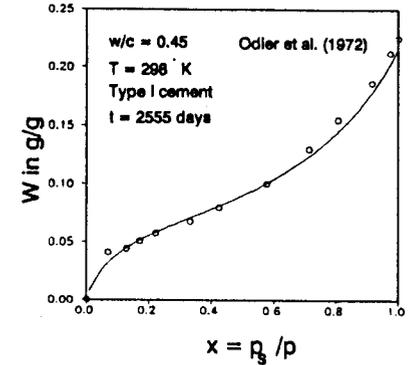


Fig. 2

Comparison of test data with prediction curves

Figs. 1-2 show comparisons of the calculated curves of the present empirical formulae with the test curves. It is obvious that for different curing times, different  $w/c$  and various cement types, these curves agree closely. Therefore it is confirmed that the chosen governing parameters, that is  $t$ ,  $w/c$ , cement type, and  $T$ , represent the major factors affecting the characteristics of the adsorption isotherm of portland cement paste reasonably well. It is also confirmed that the present empirical equation for adsorption isotherm can represent the adsorption isotherm over the complete pressure range  $p/p_s = 0$  to 1. Then, the moisture capacity, defined as  $\partial W/\partial H$ , can be obtained from the equilibrium adsorption isotherm

$$\frac{\partial W}{\partial H} = \frac{CkV_m + Wk[1 + (C - 1)kH] - Wk(1 - kH)(C - 1)}{(1 - kH)[1 + (C - 1)kH]} \quad (5)$$

## 3 Diffusivity and Diffusion Mechanisms

Water diffusion in concrete occurs by one or more of the following three mechanisms: (1) ordinary diffusion, (2) Knudsen diffusion, and (3) surface diffusion. When multiple mechanisms occur, their effects do not necessarily combine in a simple manner. Previous investigators obtained some models for each mechanism individually. Since they based their results upon diffusion in regular cylindrical pores, a tortuosity factor was introduced to take into account pore irregularity. Then the contributions of each mechanism were combined (Daian, 1988). However, as mentioned in the previous section, the pore structure changes when the water-cement ratio changes. Also the formation process of fine micropores is strongly time dependent and humidity level dependent. Therefore, it is difficult to obtain a general expression for diffusivity. The model we will now present does not treat each mechanism individually, but tries to predict the general combined trend.

Upon comparison of all the three diffusion mechanisms, it is clear that they share similarities. At low humidity, the pore volume decreases, the field force weakens, and the mean free path decreases. These behaviors may just offset each other such that the effective diffusivity for all the mechanisms combined become approximately constant at low humidity (see Fig. 3). At high humidity, capillary condensation occurs, and so the

diffusion resistance lessens. Consequently, the effective diffusivity of the system may be assumed to follow the simple empirical curve shown in Fig. 3. The inevitable empirical aspect of this curve makes it unnecessary, and in fact unjustified, to distinguish among these mechanisms. A simple formula that reflects the aforementioned trends is

$$D_h = \alpha_h + \beta_h \left[ 1 - \exp \left( -10^{\gamma_h(H-1)} \ln 2 \right) \right] \quad (6)$$

where  $\alpha_h, \beta_h,$  and  $\gamma_h$  are coefficients to be calibrated from test data (Fig. 3 displays their meanings).  $\alpha_h$  represents the lower bound on the diffusivity approached at low humidity levels. The value of  $\beta_h/2$  is the diffusivity increment from a low humidity level to the saturation state.  $\gamma_h$  reflects the humidity level at which the diffusivity begins to increase.

The coefficients  $\alpha_h, \beta_h,$  and  $\gamma_h$  are strongly affected by  $w/c$ . The effect of curing time on these coefficients could be regarded as negligible. However, the curing time actually does affect the diffusion process. Its effect is accounted for when the moisture capacity is considered.

Before calibration by test data, the possible relations between  $\alpha_h, \beta_h, \gamma_h$  and  $w/c$  must be analyzed. As described earlier, the porosity increases as  $w/c$  increases. This means that the volume fraction of macropores increases, too. As a result, the diffusivity at low humidity levels increases with increasing  $w/c$  because water molecules migrate much faster in the macropores than in the micropores. Thus,  $\alpha_h$  generally increases with increasing  $w/c$ .  $\beta_h$  first increases with increasing  $w/c$ , for the same reason as  $\alpha_h$ . After a certain point, however,  $\beta$  decreases with increasing  $w/c$  because the increase of diffusivity from a low humidity level to the saturation state will decrease gradually with an increasing volume fraction of macropores. An increase in  $w/c$  leads to an increase in  $\gamma_h$ . From Fig. 3, a larger  $\gamma_h$  corresponds to a higher humidity level at which the diffusivity initially begins increasing, and it also corresponds to a higher rate of diffusivity increase. This trend is reasonable because a higher  $w/c$  corresponds to a larger volume fraction of macropores, and the humidity level or the pressure level that is necessary for the capillary condensation is higher in a larger pore than in a smaller pore, according to the theory of capillarity. Knowledge of the foregoing general trends is helpful to choose a correct function to be calibrated by drying test results.

Eq. 1 is solved by the finite difference method, using the Crank-Nicolson algorithm, for both cylindrical and Cartesian coordinate systems.  $D_h$  (Eq. 6) is a function involving unknown parameters  $\alpha_h, \beta_h$  and  $\gamma_h$ . Therefore, a nonlinear curve-fitting program is used and the program for the finite difference solution is combined with a nonlinear optimization subroutine in order to calibrate the three parameters by available test data.

The optimum formulae for  $\alpha_h, \beta_h$  and  $\gamma_h$  are

$$\begin{aligned} \alpha_h &= 1.05 - 3.8 \frac{w}{c} + 3.56 \left( \frac{w}{c} \right)^2, & \beta_h &= -14.4 + 50.4 \frac{w}{c} - 41.8 \left( \frac{w}{c} \right)^2, \\ \gamma_h &= 31.3 - 136 \frac{w}{c} + 162 \left( \frac{w}{c} \right)^2 \end{aligned} \quad (7)$$

The theoretical prediction curves based upon moisture capacity (Eqs. 2-5) and diffusivity (Eqs. 6-7) are shown in Figs. 4-6 in comparison with the test data. All the theoretical curves fit the test curves satisfactorily and give reasonable long-term predictions as well.

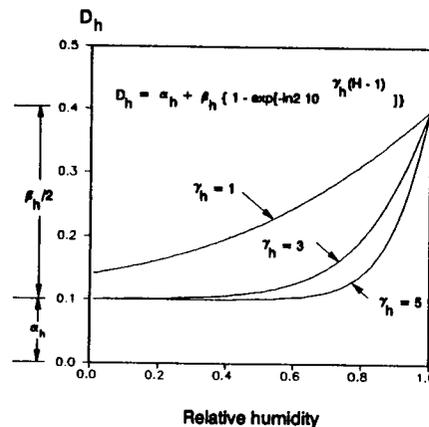


Fig. 3 Diffusivity

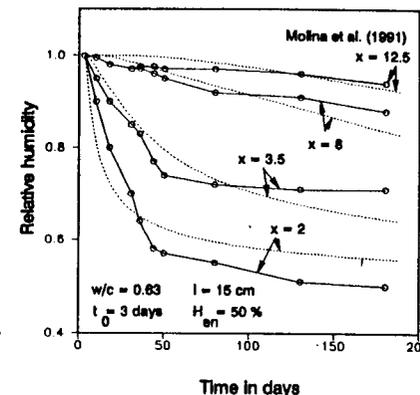


Fig. 5 Comparison of prediction curves with test results

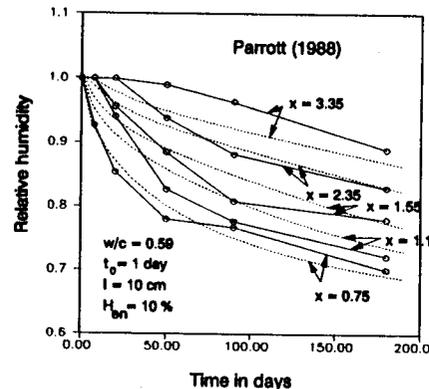


Fig. 4 Comparison of prediction curves with test results

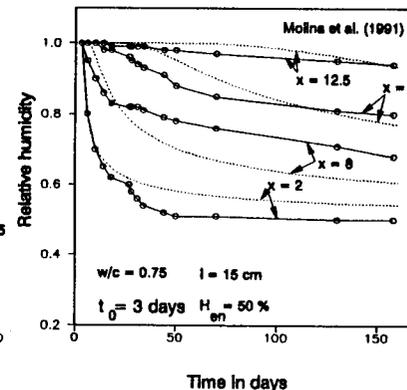


Fig. 6 Comparison of prediction curves with test results

#### 4 Summary and Conclusions

1. The concrete drying process can be described by the diffusion equation governing the pore relative humidity. The moisture capacity and diffusivity in the diffusion equation should be treated as two separate coefficients and evaluated by independent test results. Both the moisture capacity and diffusivity are dependent on the pore structure of concrete, and the pore structure depends upon the basic material parameters, such as the water-cement ratio, the curing time, temperature, and the type of cement.

2. The BSB model is chosen as the prediction model for the adsorption isotherms. Some empirical formulae are established for determining the three parameters of this model based on the available adsorption test data. The calculated results show that the present empirical formulae can simulate the parameters quite accurately and therefore can predict the adsorption isotherms for various portland cement pastes well.

3. There are three possible diffusion mechanisms for concrete drying: ordinary diffusion, Knudsen diffusion, and surface diffusion. By individual analysis of each diffusion mechanism, the common features of the mechanisms are found: for low humidities, the diffusivities may become constant, and at high humidities, the diffusivities increase, regardless of mechanism. Therefore, instead of considering combinations of the diffusivities for various mechanisms, a total diffusivity expression that simply reflects these common features is proposed.

4. The influence of water-cement ratio on diffusivity is analyzed. With increasing  $w/c$ , (1) the diffusivity at low humidity level increases, (2) the incremental part of diffusivity increases up to a certain value, then decreases and vanishes asymptotically with very large  $w/c$ , and (3) the humidity level at which diffusivity begins increasing becomes higher.

5. The present model for moisture diffusion through concrete gives satisfactory diffusion profiles and realistic long-term predictions.

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